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THE UNIVERSITY OF ALBERTA

"LOWER DEVONIAN BENTONITES FROM GASPE, P.Q."

A DISSERTATION

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

FACULTY OF GRADUATE STUDIES

DEPARTMENT OF GEOLOGY

by

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A B S T R A C T

Samples of six bentonites from Shiphead, Gaspe, P.Q., have been collected with the aim of obtaining from them minerals datable by the K/Ar method. The literature on the biostratigraphic age has been reviewed and the conclusion reached that these beds lie in the Onesquethaw Stage of the type section of the U.S.A., and the Lower Coblenzian sub-stage of Europe.

In the course of a detailed petrological study of the bentonites, the presence of three minerals that might be reliable for absolute dating - sanidine, biotite and zircon - has been revealed, and the K/Ar method applied to the first two of these. An average age of 386 m.y. ($\pm$5%) has been obtained, a figure which is in accord with other Devonian ages recently reported elsewhere.

The petrological study has shown that the bentonites are now made up largely of a randomly interstratified mixed layer illite-montmorillonite clay, with lesser amounts of cryptocrystalline quartzo-feldspathic material, and minor amounts of holocrystalline minerals. Attention has been drawn to the presence of minerals that can only be regarded as con-

taminants, and the significance of these evaluated. Total chemical and minor element (Ba) analyses have been used, in conjunction with the modal composition to suggest trachytic or rhyolitic affinities for the source materials. The development of certain authigenic minerals has been used to draw limited conclusions regarding the chemical environment in which diagenetic changes took place.

Finally sanidine obtained from the uppermost bentonite has been compared chemically and optically with six others used for absolute dating purposes.

A C K N O W L E D G M E N T S

The writer wishes to register his gratitude to all staff members of the Department of Geology for their helpful suggestions, particularly Dr. R.E. Folinsbee who has supervised the work, and Dr. H. Baadsgaard and Dr. K.A.W. Crook who have given generously of their time in discussing various aspects of this investigation with the author.

The field work at Cape Gaspe was made more enjoyable and considerably easier by the kindness and hospitality of the Minchinton family at Shiphead.

The research on which this report is based has been generously supported from several quarters. The K/Ar dating project at the University of Alberta has been financed by grants from the Geological Society of America and the University of Alberta Research Fund, whilst the National Research Council has greatly assisted in the setting up and maintenance of a mass spectrometer in the Department of Physics. The author would like to express his gratitude to the Geological Survey of Canada, whose financial assistance has made possible his work as a graduate student at the University of Alberta.

Finally, thanks are due to F. Dimitrov for his aid with the photographic work, and to my wife for her typing and secretarial work.

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F R O N T I S P I E C E

An aerial view looking northwest along the Forillon peninsula. The bentonites outcrop directly below the lighthouse seen in the left foreground. The cliffs on the northeast side of the peninsula are made up largely by the Forillon Member, whilst the ridge on which the lighthouse stands is composed of rocks of the Shiphead and Indian Cove Members.

I N T R O D U C T I O N

The primary purpose of this study has been to determine the absolute age of a biostratigraphically well dated horizon in the Lower Devonian. To this end, samples of six bentonites occurring at Shiphead, Cape Gaspe (see Figs. 1 and 2) were collected and systematically examined for minerals that would allow such an age to be determined - and in particular for the potassium-bearing minerals sanidine and biotite.

In the course of the work, a number of other aspects of the bentonites have, however, been investigated in the hope that they might throw new light on the nature of the source material, provenance and diagenesis.

PREVIOUS WORK

Even today only small areas of Gaspe are thoroughly investigated geologically, despite the fact that a number of famous men have worked in the area since Sir William Logan's pioneer work in 1843 and 1844. The findings of these workers having bearing on this thesis are summarised in the chapter on stratigraphy.

In 1957 L.S. Russell, formerly with the Quebec Department of Mines, drew the attention of Folinsbee to the occurrence at Shiphead of a number of bentonite beds within the Shiphead Member of the Lower Devonian Grande Greve Formation. In the following year Folinsbee made a reconnaissance trip to the locality and collected samples of six such beds. Cursory examination of this material did not reveal the presence of sanidine, but a small quantity of biotite and an even smaller quantity of zircon was noted. The bentonites were found to be made up dominantly of a clay mineral that was tentatively identified as illite, on the basis of the X-ray powder photograph, and relatively high K_2O content (4.89%). This mineral yielded an absolute age of 342 m.y. for the bed (Folinsbee et al, 1960b). It was at this stage that Folinsbee, recognising the rather unsatisfactory nature of the mineral used for dating, suggested to the author the further research upon which this thesis is based.

Other absolute dating work at this stratigraphic level has been confined almost entirely to the dating of Acadian intrusions of eastern North America (Alcock, 1935; Hurley, et al, 1958). Such dates, by the nature of the field relations, can give only the minimum age of the sediments intruded and maximum age of those unaffected.

A considerable amount of work has been carried out on the iron potassium clay mineral glauconite, which it was considered might provide a means of dating sediments. However, it has gradually become apparent as Holmes (1959) has pointed out, that glauconite is highly sensitive to the chemistry of its environment, and gives somewhat erratic, and generally low, results.

Lava flows and pyroclastic deposits offer the only other alternatives so far discovered of dating sedimentary sequences. The former, when containing potassium minerals, are usually acid in character and therefore viscous and of restricted areal extent.* Pyroclastics, however, may be distributed over wide areas. The absolute dating project at the University of Alberta has been concerned mainly with the investigation of such rocks, ranging in age from Ordovician to Tertiary, and has demonstrated not only the common occurrence of

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* Little work has as yet been done, it appears, to investigate the potentialities of the more basic K-rich lavas, such as leucite trachytes.

the potassium minerals required for absolute dating, but also their potentialities in giving accurate ages to the parent rock (Folinsbee et al, 1960a). Although this University is at present equipped only for determinations based on the K/Ar method, it has been demonstrated in other institutions that the ages obtained may be cross checked by the Rb/Sr method (Faul, personal communication to Baadsgaard) or by the U^{238}/ Pb^{206} method utilizing the cogenetic zircon that is frequently present (Edwards et al, 1959).

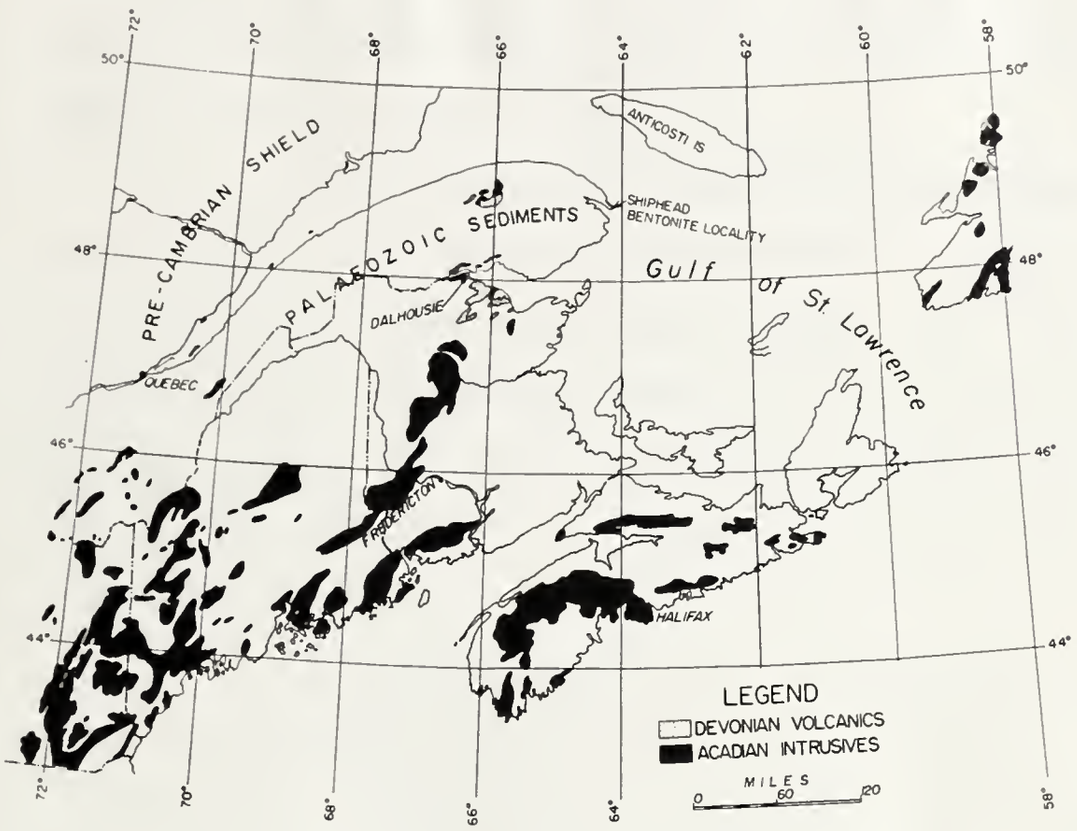
72°
70°
68°
66°
64°
62°
60°
58°
50°
48°
46°
44°
ANTICOSTI IS
SHIPHEAD
BENTONITE LOCALITY
PRE-CAMBRIAN SHIELD
PALAEOZOIC SEDIMENTS
Gulf of St. Lawrence
DALHOUSIE
QUEBEC
FREDERICTON
HALIFAX
LEGEND
DEVONIAN VOLCANICS
ACADIAN INTRUSIVES
MILES
0
60
120

FIGURE 1.

S T R A T I G R A P H Y

The Lower Devonian sequence of Gaspe was one of the first studied by Sir William Logan in his pioneer work for the Geological Survey of Canada in 1843 and 1844. The Gaspe Peninsula has since been the subject of several geological investigations and a good bibliography has been given by Cumming (1959).

Logan divided the rocks of eastern Gaspe into three units. The second of these units, the Gaspe Limestone Series, he subdivided (Logan, 1863) into eight members on a lithological basis. It is a tribute to Sir Williams's work that these eight members are, with only minor modification, used by most recent workers in the area.

The following discussion is concerned mainly with the Shiphead Member (Logan's number seven) of the Grande Greve Formation, the latter being one of three formations into which Clarke (1900) divided Logan's unit number two.

In view of the nature of the present investigation it is necessary to review in some detail the opinions of previous workers on the biostratigraphic age of the Gaspe Limestone Series and in particular the Shiphead Member. Logan (1863) referred the series to the Upper Silurian. Billings (1874) placed Members 1 and 2 in

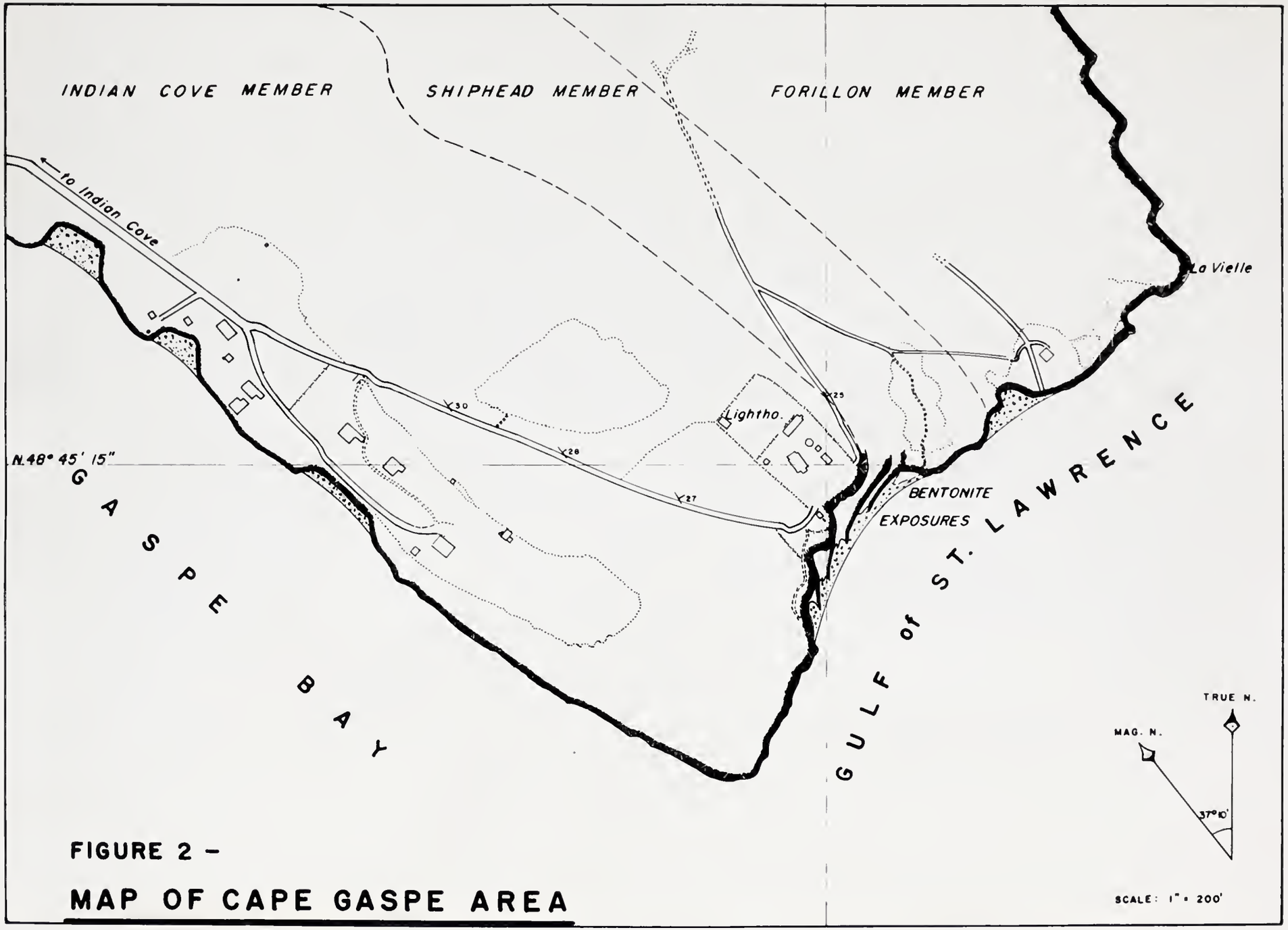

FIGURE 2 –

MAP OF CAPE GASPE AREA

the Upper Silurian (i.e. in the Helderberg group which at that time was considered to be of Silurian age) and Members seven and eight in the Lower Devonian. Intermediate members were designated "passage beds." Ells, (1883) compared the faunas of the Forillon and Perce sections and suggested an Oriskany age for the beds. The following year (Ells, 1884) he ascribed the first six of Logan's members to the Upper Silurian and Lower Helderberg, and 7 and 8 to the Lower Devonian.

Clarke was the next person to work in the area. After reviewing previous work he carried out a detailed faunal study and in 1908 published a large volume including 48 plates of fossils. He considered that the fauna of Members 7 and 8 was dominantly Oriskany but had some Helderbergian aspects. The St. Alban fauna was dominantly Helderbergian with insignificant Oriskany elements and the Cap Bon Ami a mixed, reduced and diminutive fauna, intermediate between St. Alban and Grande Greve. In 1913, whilst retaining the lower part of the Grande Greve as Oriskany, Clarke regarded the upper portion (presumably Member 8) as of post-Oriskany age.

Cooper et al (1942) indicated the St. Alban as Helderbergian; the Cap Bon Ami Formation, on the basis of a few Helderberg fossils, was tentatively placed in the Becraft Stage and the Grande Greve put entirely in the Deerpark Stage of the Oriskany. It was noted that some

beds even younger than those in the New York section might be present in the Gaspe region. Clarke (1908) assigned a Hamilton age to the Gaspe Sandstone Series, which lies above the Limestone Series, but Williams (1910) and later workers have disagreed with the interpretation, pointing out that Hamilton species, whilst present in wide variety, are poor in numbers and in this respect dominated by Oriskany forms. Cumming (1959) did not accept the major stratigraphic break between the Cap Bon Ami and Grande Greve Formations suggested by Cooper's committee, evidence for which would certainly appear to be scant.

Russell (1947) introduced eight Member names for the Gaspe Limestone Series, and these have won acceptance amongst later workers and are used here.

On the basis of the work mentioned above which is largely summarized from the review of Russell (1947), the Shiphead Member of the Grande Greve Formation is considered to be of Oriskany age, that is, at the top of the Lower Coblenzian sub-stage of Europe. Besides the direct comparisons that may be drawn between the Gaspe faunas and those of New York and adjacent areas in eastern North America, some elements have Rhenish affinities that provide a link with the European sections. This subject has recently been critically discussed by Boucot (1960). Plate 1 shows fossils collected by the writer from the

Shiphead Member and uppermost beds of the Forillon Member, and Plate 4 microfossils obtained from the bentonites themselves.

The 1947 report of Russell gives a very comprehensive lithologic description of the Shiphead Member in which no less than 86 beds are detailed, and it is not intended here to elaborate on this. A reconnaissance visit to the locality by Folinsbee in 1958 and a further longer stay by the present writer in 1959 resulted in the positive identification of six bentonite beds ranging in thickness from 6 inches to over 2 feet, plus several very thin beds. Russell (1947) described a number of 'bentonitic shales' but only three bentonites. Several of the bentonites become shaly at the top (see page 20) and shales may be distinctly bentonitic so that it is difficult to say where the line between bentonite and shale is to be drawn. The bentonitic shale (see section on clay mineralogy) gives an X-ray pattern essentially similar to that obtained from pure bentonite. It differs however in being harder, less easily broken down in water, and in containing more carbonate. It is suggested, therefore, that such shales are formed from the weathering of volcanic material or reworking of it within the depositional basin. Such an origin would explain the observed complete variation between calcareous shale and bentonite.

The Shiphead Member has struck most previous workers in the region as being characterized by variations in lithology. Both the upper and lower boundaries are defined arbitrarily, the upper being taken at a bright grass-green calcarenite, one of a number of 'grit' beds (Russell's beds 64-84) at the top of the Shiphead Member. The usefulness of this bed as a marker horizon has however not been proved, and it has only been traced a few hundred feet inland. The mineral giving the bed its colour has been identified by Moorhouse (Russell, 1947) on the optical properties, as a chlorite. X-ray investigation by the present writer shows that a well-ordered glauconite is present, mixed mechanically with some chlorite. McGerrigle (1950) had suggested the possible presence of glauconite. The mineral offers the possibility of an absolute age determination on a different material. Whilst the value of glauconite ages is becoming more and more doubtful, if nothing else it might put a further nail in the coffin of this method.

After the striking colour of the grit zone, the abundance of chert and cherty limestone in the Shiphead sequence impresses a person most. The source of the silica in these rocks has been the object of a good deal of speculation. Parks (1929-1930, p.32) favoured a derivation from volcanic ash erupted from volcanoes "known to exist in Lower Devonian times to the Westward," whilst other writers prefer to look to Silurian volcanics as the

source. Clarke (1908, pp.270-271) observed that beds several inches thick are made up of matted masses of sponge spicules. No thorough investigation of the source of the silica has however been carried out, and a detailed study in the light of recent work on silica in sediments might well provide more conclusive evidence.

Russell (1947) draws the lower boundary of the Shiphead Member about 9 feet below the base of the lowermost bentonite. The present writer would lower this boundary several feet to the top of another greenish grit zone which overlies a very fossiliferous chocolate-brown to grey-brown limestone bed. This grit zone is a good deal thinner than that at the top of the Shiphead Member (about 4 feet) and the greenish colour much less distinct. Both probably represent periods of shallowing of the basin. The chocolate-brown limestone, together with another horizon a few feet lower,* furnished most of the specimens shown in Plate 1.

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* This bed is well exposed about 100 yards up the small stream that runs into the bay on the northeast side of the promontory by which descent to the head is made.

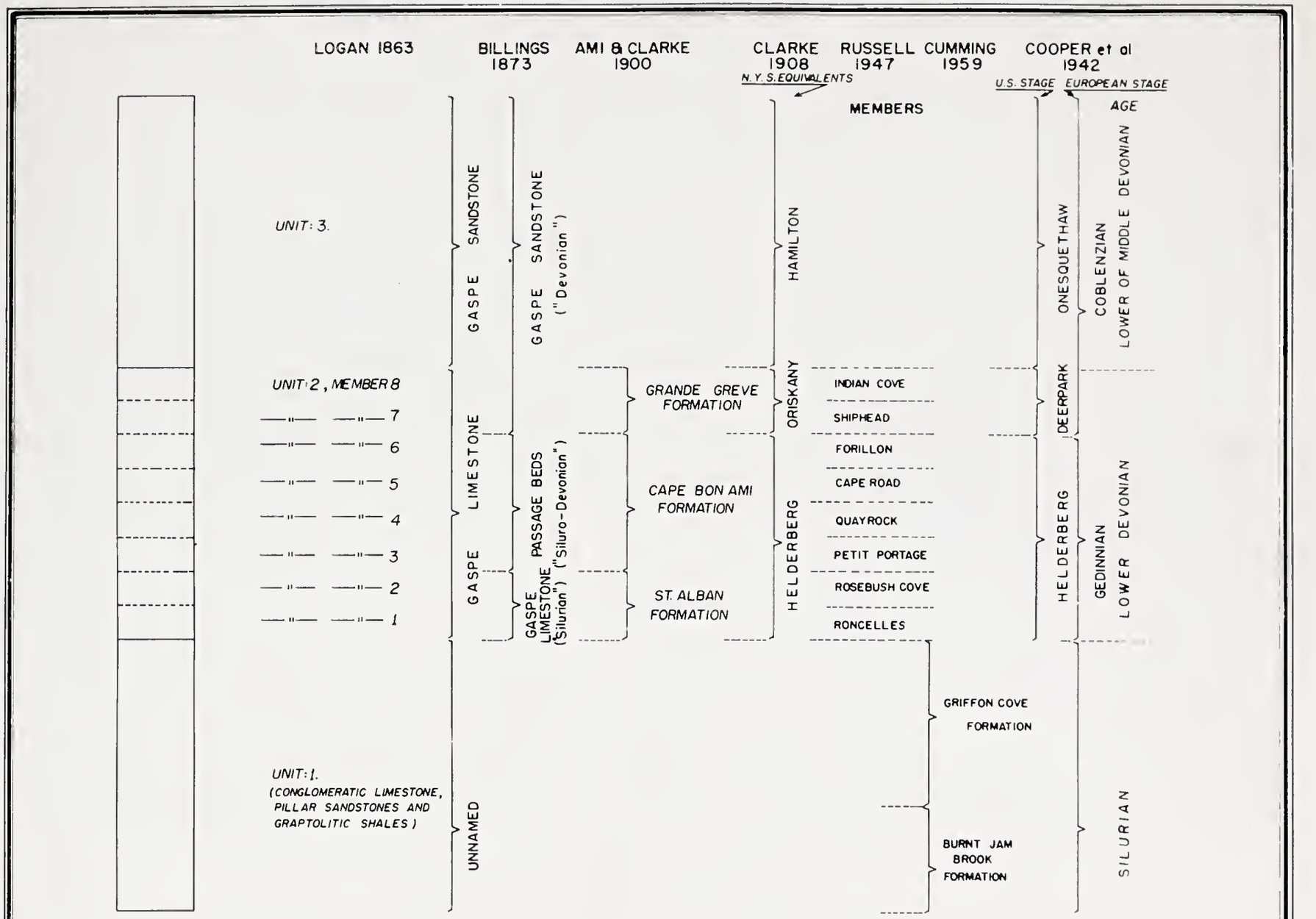

FIGURE 3. STRATIGRAPHIC NOMENCLATURE AND CORRELATION OF THE FORILLON SECTION.

FIGURE (4)

Left:- The Shiphead succession at the bentonite locality, Cape Gaspe (see also Figs. 1 and 2). The lowermost bentonite meets the beach in the near foreground and the uppermost behind the first promontory. The headland in the distance is formed by rocks of the Indian Cove Member, and the "grass-green grit" - the uppermost bed of the Shiphead Member - lies at its base.

Right:- View of the cliffs formed by the Shiphead and Forillon Members at Cape Gaspe. The promontory by which descent is made to the beach and from which the photograph (left) was taken, is in the foreground. The base of the Shiphead Member lies on the far side of this promontory.

FIGURE 4.

PLATE (1)

Fossils from Shiphead and Forillon Members

1. Leptostrophia magnifica HALL, interior of dorsal valve. (Natural size). Uppermost Forillon Member.

2. Leptostrophia magnifica cf. var. tullia (BILLINGS), cast of ventral valve showing character of muscle scar. (Natural size). Uppermost Forillon Member.

3. Leptostrophia blainvillii (BILLINGS), cast of ventral valve showing character of muscle scar. (Natural size). Uppermost Forillon Member.

4. Chonetes canadensis BILLINGS, cast of interior of dorsal valve showing the cardinal process and very long oblique sockets and socket walls. (Natural size). Uppermost Forillon Member.

5. Meristella champlaini CLARKE, posterior view. (Natural size). Uppermost Forillon Member.

6. Meristella champlaini CLARKE, dorsal view. (Natural size). Uppermost Forillon Member.

7. Dalmanites perceensis CLARKE, pygidium showing sulcate ribs, coarse irregularly placed nodes on lateral lobes and paired nodes on medial lobe. (Natural size). Shiphead Member.

8. Fish scale. (Natural size). Uppermost Forillon Member.

9. Meristella lata HALL, dorsal view. (Natural size). Uppermost Forillon Member.

10. Platyceras tortuosum HALL. (Natural size). Shiphead Member.

11. Favosites cf. limitaris. An individual showing polygonal outline of corallites. (Natural size). Uppermost Forillon Member.

12. Diaphorostoma desmatum CLARKE. (Twice natural size). Shiphead Member.

13. A cyathophylloid coral, showing budding. (One-half natural size). Uppermost Forillon Member.

PLATE : I.

14. Beachia amplexa CLARKE, cast of interior of ventral valve. (Five-fourths natural size). Shiphead Member.

15. Actinopteria commemsi (HALL), internal view of the left valve. (Twice natural size). Shiphead Member.

16. Spirifer cf. murchisoni CASTELNAU, posterior view. (Six-fifths natural size). Shiphead Member.

17. Uncinulus sp.?, posterior view. (Natural size). Uppermost Forillon Member.

18. Uncinulus sp.?, dorsal view. (Natural size). Uppermost Forillon Member.

19. Beachia cf. amplexa CLARKE, dorsal view. (Natural size). Uppermost Forillon Member.

P E T R O L O G Y

GENERAL STATEMENT

It was felt that a petrological study of the Gaspe bentonites would serve several useful purposes. It should confirm the volcanic origin of the rocks, give an indication of the character of the source material, show which bentonites contained minerals suitable for absolute dating, and finally show whether the deposits are contaminated by detrital material of non-volcanic origin.

Thin sections of the bentonites showed that the beds are made up very largely of clay minerals. These were separated from sand size* material and the two studied independently.

The method employed to separate the two fractions is described on page 114. Here also are explained techniques used to isolate particular minerals required for dating purposes. It was found that examination of each of the separates obtained by these techniques, and of

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* The terms "sand size", "sand fraction" etc., are used in this thesis to refer to the residue after breakdown of the raw material and removal of the clay minerals. This residue includes all grain sizes down to the U.S. sieve mesh number 325, and thus, strictly speaking includes a part of the silt grades.

another containing all heavy minerals (obtained by a standard separation of a portion of the sample in tetrabromoethane, without magnetic fractionation), was sufficient to disclose both major and minor sand size constituents.

Apart from microscopical examination of these mineral separates, and study of thin sections, an X-ray examination of the clay fraction of each bentonite was made, a total chemical analysis carried out in the case of the uppermost bentonite, and each of the beds analyzed for barium (see p.62).

FIELD SAMPLE DESCRIPTIONS

BENTONITE NO. 1 (3854-1):- The bed is a light grey-green bentonite at least 2 feet 5 inches thick. The upper surface is regular with no sign of any erosion having taken place. The uppermost layers are thin and shaly (a characteristic of all the bentonites) while approximately 15 inches from the top is a particularly hard band, about 8 inches thick.

BENTONITE NO. 2 (3854-2):- This bed is 14 inches thick and rather poorly exposed having receded to some depth into the cliff, between the limestone posts above and below. It varies in colour from grey at the top (where it is rather harder and more shaly) through kahki in the centre to yellow brown (in places) at the base.

BENTONITE NO. 3 (3854-3):- The bed is 12 inches thick and also poorly exposed. It is somewhat darker in colour than Nos. 1 and 2. The roof is smooth with no sign of erosion.

BENTONITE NO. 4 (3854-4):- Somewhat thinner than the other beds, it pinches and swells but averages about 6 inches. Much of the bed appears to be rotted to either a yellow or a duck-egg-blue plastic clay, and at or near the centre there is a layer of what appear to be concretionary nodules. The upper surface is hardened and looks very much like some of the shale in the sequence. Again, the exposure is very poor and the material difficult to obtain.

BENTONITE NO. 5 (3854-5):- This is 14 1/2 inches thick and has smooth upper and lower surfaces. It is dark olive green in colour except for a few pods of 'rotted' yellow-coloured material. The surface of the underlying limestone is covered with grains of quartz(?) and a flaky, black mineral which is probably biotite.

BENTONITE NO. 6 (3854-6):- The total thickness of this bed was not determined because of the scree covering. However it is at least 1 foot 6 inches and may be as much as 2 feet 6 inches. The bed is a dark olive green colour,

and shows the conchoidal fracture and waxy appearance better than any of the other beds. The upper surface is smooth.

SHALE (3854-sp.3):- The No. 4 bentonite is overlain by a limestone with a shaly weathering surface. The shaly appearance becomes more prominent upward, until 5 feet 6 inches from the bed are 6 inches of shale having many similarities with the bentonite beds. The main differences in fact are the fissility and the harder, more lithified, character of the shale. Concretionary nodules are present in the bed.

CALCARENITE (3854-sp.19):- This is a bright green rock containing carbonate and possibly quartz and feldspar fragments set in a green coloured matrix that could be glauconite or chlorite. Fossil material is also present. The bed lies one foot below the top of the Shiphead Member.

FIGURE (5)

Above:- Shows the typical recessive character of the bentonites, in this case, beds 4 and 5.

Below:- A close-up of No. 4 bentonite showing the uneven character of the upper surface.

FIGURE 5.

FIGURE (6)

Above:- A close-up of the No. 1 bentonite, the thickest of the six. This bed has least fissility and displays the conchoidal fracture well.

Below:- A close-up of the No. 5 bentonite which shows rather more fissility. Here upper and lower contacts are smooth.

FIGURE 6.

FIGURE (7)

Top left:- Bentonite 3854-1 seen in thin section cut across the bedding. Several grains of quartz and feldspar are visible. Crossed nicols, magnification X 175.

Top right:- Bentonite 3854-6 seen in thin section cut across the bedding. The latter is clearly picked out by the preferred orientation of the clay mineral flakes with their C-axis perpendicular to the bedding, and runs from the top right to bottom left-hand corner of the photograph. Crossed nicols, magnification X 175.

Bottom left:- Thin section of the "grass-green" calcarenite taken as the top of the Shiphead Member. The light grey mineral is carbonate and the darker grey material in patches and in the interstices is the chlorite-glauconite clay mineral mixture. The near white grains are quartz and feldspar. Seen under P.P.L. Magnification X 175.

Bottom right:- Bentonite 3854-1 seen in thin section cut parallel to the bedding. The large area of the slide in extinction is due to the preferred orientation of individual clay mineral flakes with their C-axis perpendicular to the bedding. Crossed nicols, magnification X 450.

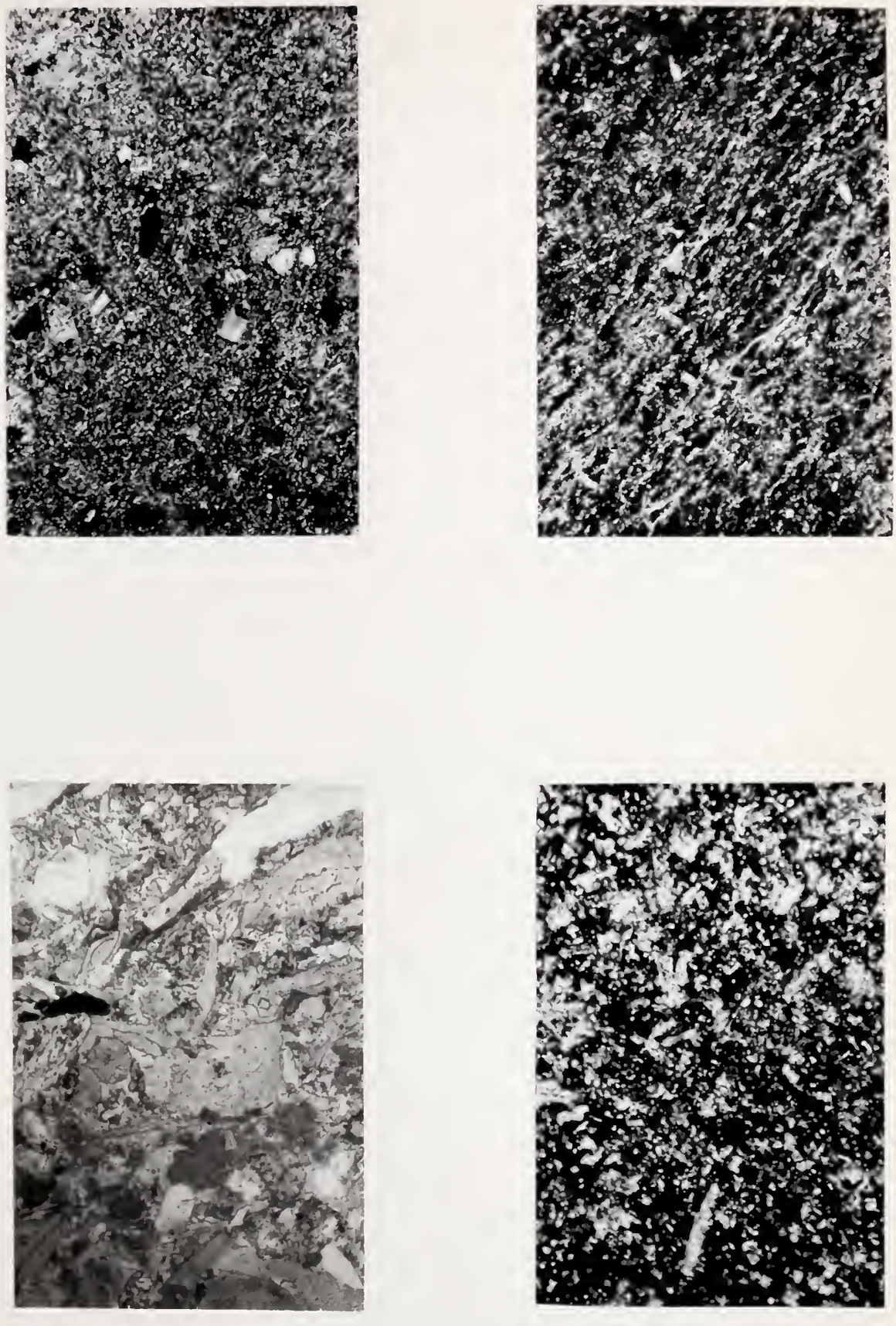

FIGURE 7.

COMPOSITION OF THE SAND FRACTIONS

3854-1:-

This bentonite furnished the most complex suite of minerals, the interpretation of which is not without its problems.

As is the case with all the bentonites quartzo-feldspathic aggregates are absolutely predominant. These are composite grains made up of merocrystalline patches of quartz and feldspar. Sometimes one of these areas is large enough and sufficiently well crystallised to give a poor interference figure allowing positive identification of both quartz and feldspar. However, the boundaries between the species are seldom, if ever, sharp so that one mineral appears to grade into the other. Clay minerals are intimately associated with the aggregates and sometimes appear to replace them in part. It is believed that the aggregates represent nuclei of crystallization formed prior to or at the time of the volcanic eruption, and the fact that they have not been altered to clay minerals is a reflection of their semi-crystalline character. The glass (originally forming the bulk of the ash fall) has, however, been converted to clay. Thus areas of the aggregates initially made up of glass have also altered to clay.

The sanidine in this bentonite is usually clear, free of inclusions and unaltered. However, it is dominated

by unaltered albite with a maximum refractive index somewhat less than that of Canada Balsam and with a large positive 2V (probably greater than 70°). Mostly the albite is untwinned but a few grains show poorly developed albite lamellae and the maximum symmetrical extinction angle observed was about 10°, but so few grains were available for this determination that the angle may well be somewhat larger. The albite is full of inclusions - bubbles, rods and other minerals - making it easy to distinguish from the sanidine. However, some of the feldspar is rather poorly crystallised, giving patchy extinction, and in these cases positive identification is difficult.

Quartz is about as abundant as feldspar. Most grains are full of very small inclusions, and it is difficult to determine whether these are bubbles or mineral particles. Certainly bubble trains are not apparent. Folk (1959, p.68) noted that volcanic quartz is usually free of inclusions and water clear, but goes on to add that " .... bits of volcanic glass or aphanitic volcanic groundmass may be trapped ....". Complete grains exhibiting the β quartz habit do not appear to be present, and most of the grains are of irregular shape and sub-rounded rather than angular. Other material found in the non-magnetic portion of the 'light' fraction of the rock includes carbonate fragments, chalcedonic and

ankeritic sponge spicules, and a few spores.

Apart from the quartzo-feldspathic aggregates, grains of chlorite are the most common constituents of the 'light' fraction. These have a specific gravity slightly lower than tetrabromoethane and are fairly magnetic. Some of the chlorite has clearly formed from biotite, the euhedral hexagonal form being preserved, but the major portion has a shreddy habit suggesting either pyroxene or amphibole as the parent mineral. It is interesting to note that X-ray examination shows that this chlorite has a different d-spacing from that found in the clay fraction of the same bentonite, suggesting that they are of different origin. The chlorite has $2V(-) = 30^{\circ}$ to 35° (compared with a 2V of about 15° in chloritized biotite flakes).

The heavy mineral fraction of the bentonite is particularly interesting. Zircon, barite, apatite and rutile are all common and a few grains of brookite are also present. The zircon shows a very wide range of habit from the slenderest gem quality needles to stumpy crystals with pyramid but no prism faces (Plate 2). Zoned crystals are rather common, as are also grains that are well rounded, sometimes so much so that they might well be of the third cycle. Perhaps significantly no hyacinth zircons were observed. Inclusions, usually of the bubble or rod type, are ubiquitous and pitting is

very common. However no budding was noted.

Barite usually occurs as euhedra or broken euhedra and frequently exhibits zoning of the inclusions, the latter are nearly always very abundant and follow cleavage traces when not in zones. The relatively large dimensions attained by some of the crystals together with the unrounded appearance, euhedral habit, and abundance of inclusions indicate that the mineral is of authigenic origin.

Apatite is present both as euhedra, showing prism or basal pinacoid sections, and as irregular grains. The mineral is choked with inclusions, and both euhedral and anhedral grains frequently have an irregular over-growth in optical continuity (Plate 3). If it is assumed that the apatite was originally volcanic and that the anhedral grains result from breaking up of euhedra, then an over growth on all types of grain must indicate that this rim is of authigenic origin.

Rutile needles and fragments are among the less common heavy minerals. They appear opaque under normal illumination but show a deep golden yellow colour if the intensity of the light is increased. Geniculate twins are found occasionally (Plate 3).

Biotite occurs both fresh and chloritized. However, no partly chloritized grains can be observed and this suggests that the two are of different origin.

Furthermore, it is noticeable that fresh grains are frequently euhedral, while the chloritized grains are always anhedral. A standard separation in tetrabromoethane leaves most of the chloritized material in the light fractions, and the fresh material in the heavy fraction.

Garnet:-

A colourless anhedral garnet is common in the magnetic fraction (at 0.3A) with specific gravity greater than 3.3. An interesting feature is the delicately etched surfaces with markings parallel to the edges of dodecahedral crystal faces (Plate 2). Etched garnets have been frequently described in the past, but there appears to be some difference of opinion as to the nature of the corroding solution. Bramlette (1929) produced the effect by leaving some grains in hydrofluoric acid. However, McMullen (1959) believed that, since other minerals such as apatite, which is unstable in acid media, exist unaffected alongside the garnet, basic conditions are more likely to produce the etching. He found that identical effects occur when grains are immersed for several days in a 1N solution of NaOH. In a recent paper by Zaporozhtseva (1960), low pH conditions (probably from 4 to 6) are considered responsible for the corrosion. The present writer feels that an environment where apatite not only exists, but has formed authigenically, favours the hypothesis that the etching solutions are

basic rather than acid.

Pyrite is present, as it is in most of the bentonites, often in very rounded grains (possibly foecal pellets) with botryoidal surfaces. Rather surprisingly, there is also bright red hematite present, a mineral that is characteristic of quite different Eh conditions (Krumbein and Garrels, 1952).

An abundant constituent in the more magnetic portion of the fraction with specific gravity greater than 3.3, is a chromium iron spinel. The presence of the spinel (which was at first mistaken for melanite garnet, the optical properties of which are extremely similar), in a bentonite bed that also contains sanidine and quartz is not readily explained. There are two possibilities: either the mineral is detrital or it is part of the sand fraction from the volcanic ash fall. If the former is true, serious doubt is cast on the belief that these bentonites are largely uncontaminated by detritus, for spinel is the most abundant heavy mineral present in the bed (with the exception of biotite). If the latter is the case, the deposit must represent more than one volcanic eruption, for quartz is relatively abundant in the bed and cannot be cogenetic with the spinel.

TABLE (1)

Comparison of X-ray data for the Gaspe spinel and two spinels listed in A.S.T.M. card index system

G A S P E S P I N E L						Card Index (3-0873) Chromite		Card Index (5-0572) Mg Spinel	
2θ in °	d in Å	I/I'	Miller Indices	$h^2+k^2+l^2$	Unit cell edge, 'a'	d in Å	I/I'	d in Å	I/I'
18.67	4.749	13	(111)	1.732	8.224	4.81	50	4.67	4
30.57	2.922	26	(220)	2.828	8.262	2.94	60	2.858	40
36.03	2.491	100	(311)	3.317	8.260	2.51	100	2.436	100
43.75	2.067	42	(400)	4.000	8.269	2.07	70	2.021	58
57.90	1.591	44	(333),(511)	5.196	8.270	1.60	90	1.555	45
63.65	1.461	51	(440)	5.657	8.262	1.46	90	1.429	58
*122.23	0.880	-	-	-	-	?0.871	30	0.8469	10
*130.43	0.848	-	-	-	-	0.848	60	0.8247	20
-	-	-	-	-	Ave. 8.265 (Discounting (111) value)	-	-	-	-

* Not visible on the diffractogram and therefore intensity not estimated.

The mineral has the following properties:-

R.I.: Greater than 1.90 (isotropic)

Colour: Brownish-black with often a suggestion of a green tinge. Thin grains and edges show the colour clearly, but thicker grains are nearly opaque

Cleavage: None apparent

Fracture: Strikingly conchoidal (see Plate 2)

Magnetic properties:
(On Frantz isodynamic separator)

Non-magnetic at 0.2A, tilt 8°, slope 20°
Magnetic at 0.35A, tilt 8°, slope 20°

X-ray data: Positive identification of the mineral was made from a powder photograph, using a Phillips camera and Cu Kα , radiation, with voltage and current setting of 35 KV 15 m.a. A powder photograph was preferred to a diffractogram for identification purposes because a small, pure sample of the mineral could be obtained by hand-picking under the microscope. (The colourless etched garnet which occurs alongside the spinel cannot be separated from it by use of the magnetic separator nor methylene iodide). However a diffractogram was also obtained, and the intensity of the peaks could be estimated more easily and accurately from this. The spinel was indexed by comparison with a known chromite, listed in the A.S.T.M. card index system, and thus the unit cell edge could be determined.

Similarity in X-ray pattern between the Gaspe spinel and the chromite is far more marked than that between it and the Mg spinel. Furthermore, the calculated 'a' spacing puts it in the chromite - berezovskite - chrom-picotite - picrochromite field of the four-cornered

diagram $FeCr_2O_4$ - $FeAl_2O_4$ = $MgAl_2O_4$. Further definition was not attempted and the mineral will be arbitrarily referred to as chromite below.

The grains are very angular and retain perfectly the conchoidal fracture, thus they have obviously been subjected to little or no abrasion. Most of the grains are between 230 and 325 mesh, and euhedra are rare. One would expect evidence of rounding if there had been fragmentation during the weathering of a chromite-bearing rock - unless the mineral came from a serpentinite, that had been intruded in a near-solid state with the cataclastic effects that are often observed. The occurrence of chromite in serpentinites of the Lady Step igneous series of the Mount Serpentine area has been noted (Alcock, 1926, p.138) and these rocks are considered to be Lower Devonian or later in age (McGerrigle, 1950, p.103). Since they outcrop less than 35 miles from the Gaspe locality, it is unlikely that any significant rounding of the material would have taken place before deposition.

If, however, detrital origin is contemplated, there remain the questions of why the chromite occurs only in the Number 1 bentonite; how it was introduced in such quantity (relative to the other heavy mineral present); why there is no other evidence of significant contamination, particularly in the feldspar fractions;

and finally why the mineral appears in only one bentonite. Even if a bentonite bed is considered to represent accumulated ash falls from eruptions taking place over a number of years, it is difficult to understand how significant quantities of extraneous sand size detrital material can be introduced when the area is one in which limestones and shales are normally being deposited.

There exists also the possibility that the chromite has been derived from the fragmentation of pre-existing serpentinite during the eruption of a later, more acid, magma from which the sanidine and quartz were derived. Other than invoking two nearly simultaneous eruptions of extremely basic and strongly acid character in the same volcanic region, this would seem to be the only satisfactory explanation.

Pyrope garnet, which can be colourless or very pale pink, is a common accessory mineral in ultramafic rocks and the etched garnet found in this bentonite may be cogenetic with the chromite. Furthermore, one may speculate that the chloritized material described above also has the same origin. Alcock (1926, p.139c) noted that chloritized pyroxene is abundant in rocks related to the serpentinized peridotite of the Mount Serpentine area of Central Gaspe, and McGerrigle (1950, p.103) stated that highly altered amphibolites, and serpentinite occur amongst the Lady Step igneous series.

The other evidence suggesting that there has been some outside contamination of the bentonite is the occurrence of well rounded zircon and also of zoned zircon. It is difficult to see why some zircons forming in the magma chamber should be zoned and others not - unless zoned varieties are the earliest and unzoned crystals formed after fluctuations causing the zoning have ceased. However the zoned crystals are not on the average any larger, as they might be expected to be if they were much earlier. Rounding has been noted even in zircons taken straight from igneous rocks (Poldervaart, 1956) and it appears possible that some of the rounded grains found in these separates could have this origin, particularly in view of the presence of 'waisted' zircons that have obviously not attained their present shape by abrasion. It is felt, however, that the zircon separate from this bentonite is not ideal for dating purposes.

If contamination of the bentonite has occurred, it is rather surprising that there is no evidence of it in the feldspar fractions, where perhaps some labradorite might be expected. Apart from albite no plagioclase is present. However, since ultramafic rocks are postulated as the source of the contaminating material, these might have been virtually feldspar-free.

Apart from those heavy minerals normally

associated with basic rocks, the rest of the mineral suite present in the bentonite is consistent with the source material being intermediate to acid in character with trachytic or rhyolitic affinities. The euhedra of zircon, apatite and biotite, and the generally unrounded nature of the mineral grains provide clear evidence for the volcanic origin of the rock as a whole.

3854-2:-

The 'light' fraction is again completely dominated by quartzo-feldspathic aggregates. Quartz is common and falls into two distinct categories. Most prominent are grains with the β habit, which are rather rounded (see Plate 3), occasionally showing re-entrant angles and corrosion hollows such as are found in the quartz of quartz porphyries. These grains have only a few inclusions, most of which are mineral particles (a few bubbles are, however, present). Contrasted with this variety, and much less common, is another that has an irregular and more angular outline and which is choked with inclusions (mainly of the bubble kind) giving the mineral a dirty appearance. Whilst the first kind of quartz is clearly a pseudomorph after the high temperature β quartz, and of volcanic origin, the second is more like vein quartz and may thus be suspected of being a contaminant.

Very little clear feldspar is present but there

strong cleavage or etching such as is encountered in garnet) can be observed, and again these have an octahedral pattern. This mineral is almost certainly a spinel, the greenish colour suggesting the variety pleonaste or ceylonite. It is concentrated in the non-magnetic fraction and is thus probably low in iron.

Also present, but much less common than the minerals already described, are zircon and apatite. The latter again appears as well developed euhedral prisms, terminated by the basal pinacoid, pyramids, or both. Inclusions of the bubble type are common, but the overgrowths characteristic of the apatite in the previous two bentonites are absent. An interesting characteristic of the euhedra of zircon is that many of them are terminated by the basal pinacoid in contrast to the zircon in 3854-1 which very rarely shows a development of this face.

3854-4:-

Quartzo-feldspathic aggregates, carbonate fragments and quartz, with the first the most abundant, make up the 'light' fraction of the bentonite. The carbonate, which occurs as angular, well crystallized grains, comes no doubt from the segregation present as a layer within the bentonite (see p. 21). The quartz sometimes has the β form and is always a clear variety with only a few bubble inclusions. Sponge spicules are

is some poorly crystallized plagioclase showing just a suggestion of albite lamellae. This material has apparently all its refractive indices less than balsam, which puts it in the albite-oligoclase range. There are also a few grains of clear sanidine. However, most of the feldspar has been partly or completely replaced by carbonate, and pseudomorphs showing the euhedral outline are common. The areas of grains that are not replaced have refractive indices less than balsam, and a biaxial negative figure with small 2V can be obtained from some, suggesting that sanidine is the feldspar being replaced. Chalcedonic sponge spicules, often with an ankeritic infilling of the axial canal, are another constituent of the 'light' fraction. However, they are far less abundant than in the Number 1 bentonite. Carbonate does not appear to be present except as mentioned above.

Barite is absolutely dominant amongst the heavy minerals and occurs as grains up to a millimetre or more in length. The euhedral form is sometimes present (particularly in the finer fractions where the crystals have suffered less damage during preparation of the material), and the grains are full of inclusions which follow all the cleavage directions, but are concentrated along the prismatic 110 cleavage. Many of the grains are bent, and for a reason which is not clear the

whole of some of these distorted grains goes into extinction at the same time, whilst other grains have patchy or undulose extinction. The size, abundance of inclusions and euhedral form are taken to indicate that the mineral is authigenic.

The next most common heavy mineral is apatite. This very often shows the euhedral form and also the development of overgrowths identical to those described from the Number 1 bentonite. Usually the apatite crystals show prismatic development with basal pinacoid termination, but a few are capped by pyramid faces.

An opaque iron (?) mineral which is orange under reflected light is quite common, and is probably limonite. Most of the few euhedral grains of pyrite that are present are of a reddish colour, and the limonite may have formed as a decomposition product of pyrite.

Zircon is present (but rare) and occurs as slender needle-like prisms. Biotite is absent.

3854-3:-

Once again the light fraction is made up dominantly of quartzo-feldspathic aggregates and in this bentonite well crystallized quartz and feldspar are absent. Spheroidal grains of chert are noticeable in the non-magnetic fractions, and some of these have an overgrowth of cryptocrystalline silica around them; in

other cases the silica is intergrown with or perhaps replacing carbonate. These grains are almost certainly a contaminant, and possibly represent reworked silicified ooliths. (Chert and cherty limestones are abundant in the Shiphead Member). Sponge spicules are present but are not common, and a few poorly preserved spores are other organic constituents.

The heavy fraction is dominated by pyrite which occurs as spherulitic pellets. Once this mineral has been removed by heat treatment and magnetic separation, barite becomes very prominent. Once again the crystals are choked with inclusions which are mainly fragments of other minerals. However, in contrast to the barite found in 3854-2 the basal cleavage is very well developed, for basal sections, often showing the six-sided outline, are very common. Furthermore, the inclusions do not appear to have any systematic arrangement within the crystals, nor is there any evidence of the distortion noted in the crystals from the previous bentonite. Carbonate is often intergrown or included within the barite.

After barite, a greenish isotropic mineral of high refractive index is most abundant. Although no complete euhedra were observed all the grains are very angular and some show octahedral surfaces. Stepped surfaces, see Plate 3, (which could either reflect a

noticeably absent.

Amongst the 'heavies', pyrite and pyrite pseudomorphs, showing perfectly developed cubes, octahedra, pyritohedra, etc., are very common. Limonite is also abundant. Non-opaque minerals are dominated by apatite, barite and zircon in that order. The apatite which, as usual, is frequently euhedral, does not have the overgrowths seen in 3854-1 and 3854-2, and is very similar to that in 3854-3. Zircon, which is also, in most cases, euhedral, is usually full of inclusions and frequently shows pitting similar to that seen in crystals from 3854-1. Barite is less abundant than in any of the bentonites described previously. Sometimes it occurs free from inclusions but at other times is full of them. Two or three grains of an unrounded euhedral colourless garnet and one of rutile were also noted.

3854-5:-

Sponge spicules are particularly common in this bed and apart from the quartzo-feldspathic aggregates are the most abundant constituent of the light fraction. A wide variety of forms are present and include monaxons, tetraxons, hexaxons and polyaxons. Unfortunately, these fossils are very delicate and are invariably broken during the preparation of the raw material, so that many of those that are identified as monaxons may actually be fragments

of more complex forms. Although most of the spicules have chalcedonic walls and an axial canal that is frequently infilled with pyrite, some are partly replaced by carbonate and yet others made up entirely of this mineral. Since only siliceous spicules possess an axial canal, and since this is detectable in some of those now composed of carbonate it is probably that most or all of the spicules were originally siliceous. Poorly preserved spores are further organic constituents. (Plate 4).

Quartz occasionally appears in the β form but most of the grains are of rather irregular habit. Bubble inclusions are quite abundant.

Two feldspars are present. An unaltered sanidine usually with bubble or rod-like inclusions and with a 2V (-) less than 20°, occurs along with the chalcedonic spicules. In the "quartz separate" another feldspar is conspicuous. This mineral, which has very few inclusions, has a 2V which approaches 90°, and it was therefore not possible to determine the sign. However, the maximum refractive index is slightly above balsam, the birefringence somewhat less than that of quartz, and albite twinning is sometimes present, although it is never well developed. These properties suggest that the mineral is in the oligoclase-andesine range of the plagioclase series. However, some of this feldspar

material has been wholly or partly replaced by carbonate.

The non-opaque heavy minerals are dominated by euhedral apatite, which has authigenic overgrowth similar to those seen in 3854-1 and 3854-2. Pyramidal termination is rather more common, and the crystals often more stumpy than those in the first two bentonites. Inclusions are again ubiquitous and mainly of the bubble and rod type.

Barite, choked with inclusions and of a similar character to that seen in 3854-2, is present and is the most common non-opaque heavy mineral after apatite. Bent crystals are again present. However the barite is far less abundant than in the Number 2 bentonite.

Zircon occurs as needle-like prismatic euhedra, pyramidal crystals, and as well rounded grains. In fact, many of the features described from the zircon of 3854-1 are present here. Once again basal pinacoid terminations are rare.

A few flakes of biotite are present, but although it is largely unchloritized, its comparative rarity makes it unsuitable for use in absolute dating. The only other non-opaque 'heavy' present is a colourless etched garnet, quite similar to that seen in 3854-1, but in this case it is not abundant, being present in even smaller quantities than the biotite.

Opaque minerals are made up largely of pyrite

and limonite. The former which is dominant, occurs as spherulitic pellets and also as perfectly euhedral crystals, all the common crystal forms being represented.

3854-6:-

This bentonite contains far more holocrystalline material than any of the others. This fact becomes immediately apparent from an examination of thin sections. Amongst the light minerals, apart from quartzo-feldspathic aggregates, quartz and sanidine are absolutely dominant. The quartz is a rather clear variety, but does contain a few bubble, bubble-train and mineral inclusions. No examples of the β habit were encountered and most grains are angular. The sanidine, which shows little sign of alteration, occurs as unrounded anhedral grains or cleavage fragments, often with bubble inclusions. The 2V (-) is usually very small varying from 0° to about 15°. Most grains show no trace of cleavage and it is thus difficult to obtain the orientation of the indicatrix and to determine whether this is high or low temperature sanidine (see p. 156). A little plagioclase feldspar, sometimes showing poorly developed albite lamellae, is also present and has a maximum refractive index slightly greater than balsam, and 2V (-) of about 75°. These factors plus the maximum (observed) extinction angle of 15°, suggest that the

mineral lies in the andesine range of the plagioclase series. However, this feldspar is far less abundant than the sanidine.

Sponge spicules and carbonate grains are other common constituents of the light fraction, but there is no evidence that the latter mineral has formed by the replacement of feldspar and it is probably of organic or chemical origin.

The heavy minerals are dominated by biotite. The crystals are seldom euhedral, and are often somewhat chloritized. However, the more altered material floats in tetrabromoethane, and by this means, and the use of a magnetic separator, a reasonably good separation can be obtained. The mineral is mainly free of inclusions, a reddish-brown colour when unaltered, and has a 2V (-) which varies from 0° to about 10° from one grain to another.

Pyrite is nearly as abundant as biotite and occurs as spherulitic pellets and as a botryoidal coating to grains of various kinds, but mainly quartzo-feldspathic aggregates, thus pulling them down into the heavy fraction during the tetrabromoethane separation. The spherulites form by the infilling of spore cases and in one instance the case could be seen breaking away from around a pellet. However, when it is still present the pyrite takes on a red oxidised appearance on account of the

colour of the chitinous(?) material forming the spore.

Most prominent amongst the non-opaque, non-magnetic heavy minerals are isotropic grains with a yellow-green colour under intense transmitted light, and golden-yellow colour under reflected light. The mineral bears many similarities to the pleonaste described from 3854-3, and is probably a similar variety of spinel.

Zircon is present but rather rare, and occurs as needle-like prisms of varying diameter, which very frequently show pitting, and the effects of corrosion. Apatite is even less common than zircon, but appears as unrounded euhedra, euhedra with authigenic overgrowths, and sometimes as perfectly rounded grains. These factors together suggest that some or all of this mineral may be present as a result of reworking of earlier bentonites. Barite is absent from this bed.

PARTICLE SIZE DISTRIBUTION

Early in the study of the Gaspe bentonites an attempt was made to obtain a size-frequency distribution curve for the sand fraction, in the hope that perhaps some limited conclusions regarding the distance of transport could be drawn. It soon became clear, however, that such a direct approach would not be fruitful. It was found that the sand fraction could

be further disaggregated if it was treated for a second time in the Waring blender. The quartzo-feldspathic aggregates that are abundant in the bentonites are intimately associated with clay minerals. In time the blender broke the aggregates apart liberating more clay and producing a different size distribution. There remained the possibility of obtaining a size-frequency curve from particular minerals such as zircon and sanidine. In the case of zircons which on first considerations seem most suitable, a number of difficulties were encountered. First of all, because of the slender needle-like habit, the very narrow diameter allows long crystals to pass through all the sieves into the pan fraction, so that the only legitimate way of carrying out such a study would be to separate the zircons by use of heavy liquids from all the fractions greater than 325 mesh, and then to 'pan' the zircon in smaller size fractions until a workable concentrate is obtained for heavy liquid separations. (The magnetic separator does not function satisfactorily for material less than 325 mesh). The sanidine does not present the same difficulties because of its habit, but in the course of separation of the feldspar for dating it was found that although there were only minor amounts present in sieve fractions coarser than 170 mesh, below this size there was a slight increase in abundance even into the fractions obtained

from the pan. In part, these very small grains may result from the breakdown of the quartz feldspar aggregates, but might equally well represent the initial size of the volcanic dust that settled.

Moreover, it is unreasonable to assume that bentonites necessarily represent the fall-out from one volcanic explosion. There are frequently numerous explosions of varying force covering a period of hours, days, months or years, during the period when a volcano is active. In such cases it would not be expected that one grain size would predominate in the resulting ash bed, but that many might be present in different abundances. It is believed then that size-frequency studies on volcanic material are of only very limited application and can only be applied with confidence where there is clear evidence that the ash fall has resulted from one explosion. Conclusions that can be drawn regarding distance of transport will be dependant on meteorological considerations and the violence of the eruption.

PLATE (2)

Heavy Minerals from the Gaspe Bentonites (Magnification X 500 P.P.L.)

1. Zircon euhedron from 3854-3, showing pitting.
2. Zircon euhedron from 3854-1, showing the rarely developed (001) face.
3. Zircon euhedron from 3854-1, showing the rarely developed (001) face, and numerous rod-shaped inclusions.
4. Zircon euhedron from 3854-1, showing the rarely developed (001) face, stumpy prismatic habit and comparative absence of inclusions.
5. Zircon euhedron from 3854-1, with two rod-like inclusions.
6. Pyramidal zircon euhedron from 3854-1, showing almost complete suppression of the prism faces.
7. Slightly corroded, long, needle-like prism of zircon from 3854-1.
8. Broken zircon euhedron from 3854-1, with very large cavity.
9. Zircon "needle" from 3854-1, showing pitting or "nibbles".
10. "Gem-quality" needle-like zircon euhedron with no inclusions.
11. 'Waisted' zircon crystal from 3854-1, believed to result from magmatic corrosion.
12. Large zircon euhedron from 3854-1, showing pitting and many inclusions.
13. Small zircon euhedron from 3854-1 with poorly developed prism faces.
14. A stumpy slightly rounded zircon crystal from 3854-1, with mineral (and bubble) inclusions.
15. A rounded, slightly corroded zircon crystal from 3854-1.
16. A zircon euhedron with numerous inclusions, from 3854-1.
17. A broken zircon euhedron with large bubble inclusion, from 3854-1.

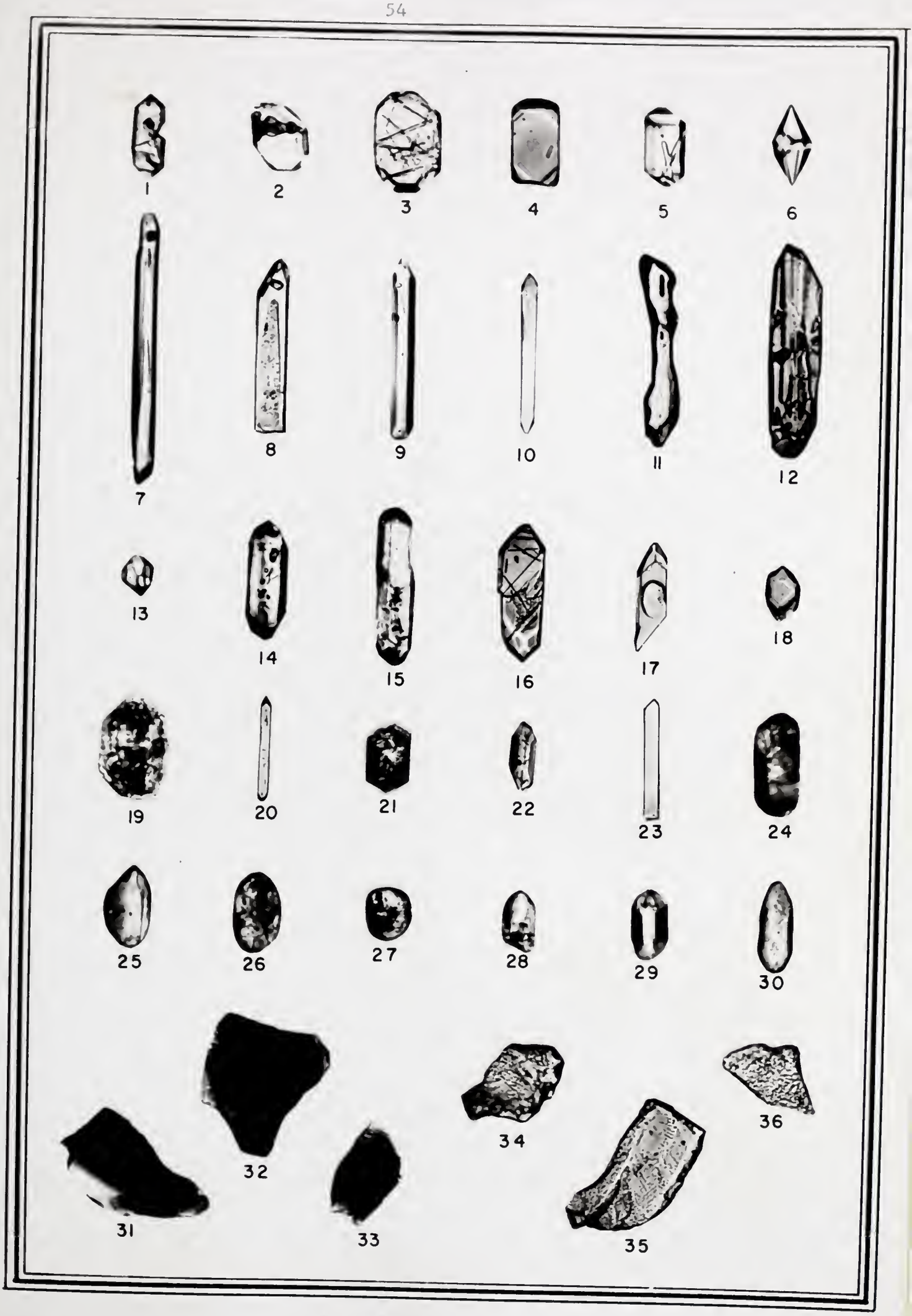
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PLATE : II.

18. A small zircon euhedron from 3854-1, showing development of prism, dome and pyramid faces.

19. A rather rounded zoned zircon crystal from 3854-1, showing development of an overgrowth.

20. A small needle-like prism of zircon from 3854-1, showing some pitting.

21. A zircon euhedron from 3854-1 showing zoning.

22. A slightly rounded and pitted zircon crystal from 3854-1.

23. A broken, gem-quality, needle-like prism of zircon from 3854-1.

24. A rather rounded rutile crystal from 3854-1.

25. A well rounded zircon crystal from 3854-1, showing pitting.

26. A well rounded zircon crystal grown around another mineral, from 3854-1.

27. A 'cannon-ball' zircon from 3854-1.

28. Well rounded zircon crystal from 3854-1.

29. A slightly rounded, stumpy zircon euhedron from 3854-1.

30. A rounded rutile crystal from 3854-1.

31-33. Anhedral grains of chromite from 3854-1 showing complete absence of rounding, a well developed conchoidal fracture surface.

34-36. Anhedral grains of garnet from 3854-1, showing delicately etched surfaces.

PLATE (3)

Minerals from the Gaspe Bentonites (Magnification X 500, P.P.L. unless otherwise stated)

1. A euhedral prism of apatite with basal pinacoid terminations, from 3854-2. The crystal is full of inclusions and has a ragged overgrowth, believed to be of authigenic origin, in optical continuity.

2. A stumpy apatite euhedron from 3854-1 with overgrowth less well developed.

3. A long prismatic apatite euhedron from 3854-2, with fewer inclusions but again with development of overgrowth.

4. A basal section of apatite from 3854-1.

5. A large stumpy apatite euhedron with narrow overgrowth, from 3854-2.

6. Apatite crystal with no overgrowth and large bubble and rod inclusions from 3854-3.

7. An overgrowth of magmatic origin around an earlier apatite crystal of the type illustrated in (3) above. From 3854-3.

8. A basal section of an apatite crystal from 3854-3.

9. Apatite euhedron with pyramidal terminal faces, from 3854-3.

10. Apatite crystal with rod-like inclusions from 3854-3.

11-17. Authigenic barite crystals showing development of euhedra, bent crystals, and arrangement of inclusions. Mainly from 3854-1 and 3854-2.

18-19. Broken, geniculate twins of rutile from 3854-1.

20. Slightly rounded six-sided flake of biotite from 3854-1.

21. Anhedral grain of pleonaste from 3854-3, showing stepped surfaces.

22. Six-sided flake of biotite from 3854-1, showing absence of inclusions.

PLATE III.

PLATE IV.

23-24. Crystals of brookite showing characteristic striated surfaces due to oscillation between vicinal faces.

25. A number of grains of sanidine from 3854-5 showing angular form and clear unaltered character. (Under crossed nicols).

26. A quartzo-feldspathic aggregate from 3854-1. Seen under crossed nicols.

27. A cluster of crystals of quartz showing the β habit, from 3854-2. These crystals, which are in optical continuity, have more inclusions than most.

28. A crystal of quartz from 3854-2, showing the β habit and the rounding of corners due to magmatic corrosion.

PLATE (4)

Microfossils from Gaspe Bentonites

1. The ostracod Walsachia, abundant in the -45 +80 U.S. sieve fraction of 3854-1. Magnification X 70.

2. Another ostracod found in the same sieve fraction as above. Magnification X 70.

3. A monaxan sponge spicule, replaced by ankeritic carbonate, from 3854-5. Magnification X 500.

4. A broken tetraxan sponge spicule from 3854-5 seen looking down fourth axis. This spicule is also replaced by ankeritic carbonate. Magnification X 500.

5. A broken hexaxon sponge spicule from 3854-4 with chalcedonic walls and pyrite infilling of axial canals. Magnification X 500.

6 - 8. Poorly preserved megaspores from 3854-1. Traces of the trilete suture can be seen in (8). Magnification X 500.

9. A megaspore from 3854-6 seen in thin section. Magnification X 500.

CHEMICAL ANALYSES

TOTAL CHEMICAL ANALYSIS:-

A chemical analysis of the 'sand fraction' from the Number 5 bentonite, carried out by the writer, gave the following results:

TABLE (2) TOTAL CHEMICAL ANALYSES

	(1)	(2)	(3)
SiO_2	68.99	74.09	73.76
TiO_2	0.17	0.18	0.12
Al_2O_3	13.83	14.85	11.98
Fe_2O_3	1.07	1.15	1.14
FeO	0.70	0.75	2.40
MnO	0.02	0.02	n.d.
MgO	2.46	2.64	0.76
CaO	2.55	2.74	0.32
Na_2O	0.43	0.46	0.53
K_2O	2.25	2.42	7.38
P_2O_5	0.08	0.09	n.d.
CO_2	0.40	0.43	n.d.
S	0.25	0.26	n.d.
H_2O	2.90	....	
H_2O^+	4.19	....	1.75
	100.26	100.08	....
(O ≡ S)	.06	.06	
TOTAL	100.20	100.02	100.48

(1) 3854-5 Gaspe sand fraction, uncorrected for water.

(2) 3854-5 Gaspe sand fraction, corrected to 100%, water free.

(3) A "potassic rhyolite", Cwm Caregog, Snowdon. (Anal. by R.J.C. Fabry) Q.J.G.S. 1927, p. 368.

The material analyzed was the residue after much of the clay had been removed by breaking down the raw material in the Waring blender and decanting the clay suspension. It is recognized that the analysis does not necessarily represent the composition of the whole bentonite. The sand fraction at this stage is made up largely of quartzo-feldspathic aggregates (which, as has already been stated are regarded as particles of rapidly chilled material and which, perhaps because of their slightly crystalline nature, have not undergone the same alteration as the more glassy material). Associated (intimately) with these is a lesser amount of clay, and it is believed, therefore, that the analysis should approach rather more closely the original composition of the ash than would have been the case had the whole rock been analyzed. It is interesting to note that Byström (1956) found rather small difference in the composition of different fractions of the Kinnekulle bentonites that she analyzed. To check this further for the Number 5 bentonite, the two major constituents (i.e. SiO_2 and Al_2O_3) were also determined for the whole rock and for the finest clay fraction. The latter shows some significant variations from the values obtained for the grit fraction but the former is in quite close agreement. (See Table (3) below).

TABLE (3) SiO_2 and Al_2O_3 analyses* for whole bentonite, sand fraction, and finest clay.

	Sand fraction	Whole bentonite	Finest Clay
SiO_2	68.99	67.91	59.78
Al_2O_3	13.83	16.02	19.76

* Uncorrected for water

The clay, which results from the alteration of the glassy portion of the volcanic ash, as discussed under the section on clay mineralogy may have been subject to some changes in chemical composition - particularly in water, alkali, and alkaline-earth content. For this reason, the analysis has been recalculated to 100% on a water free basis, and should represent more nearly the original composition of the ash.

It is impossible to determine to what extent the proportions of the alkalis and alkaline-earths have been altered, but the present composition is unusual as far as these elements are concerned. Calculation of the C.I.P.W. norm shows that the rock falls into the category Class 1, Order 2, Rang 4, Sub-rang 2, and reference to Washington's "5159 superior analyses" shows that this group is poorly represented amongst unaltered igneous rocks (for calculation of the norm see appendix). This fact could be held to indicate

that cation exchanges have taken place. Indeed, if the leaching of some K^{+} and enrichment in Ca^{++} and possibly Mg^{++} is allowed for, the rock has most of the characteristics of a rhyolite. (See Table 2). This sort of source material, furthermore, is indicated by the mineral separates from the bentonite, which were described previously (p. 48).

BARIUM DETERMINATIONS:-

The occurrence of an abundance of barite in one of the Gaspe bentonites (3854-2) and a lesser amount in others has already been noted in the section on the composition of sand fractions. The habit of the barite, unrounded, and full of inclusions, together with the absence of large amounts of other contaminants leaves little doubt that the mineral is authigenic.

The question then arises as to the source of the barium. The behaviour of barium during the crystallization of a magma is reasonably well understood by the application of Goldschmidt's rules of ionic substitution. The element having an ionic radius of 1.46 Å, almost identical to that of K (Green, 1959), and a higher positive charge, should be captured by early potassium-bearing minerals. However, the separation of such minerals begins only in the intermediate stages of normal differentiation and crystallization

of a basic magma and until this point is reached, Ba should be accumulating in the residua from previous crystallizations. The early work on the geochemistry of barium was carried out by Von Engelhardt (1936), who demonstrated quite convincingly that Goldschmidt's rules, applied in this way, gave a satisfactory explanation of the abundance of Ba in the various rocks he examined.

The first potassium minerals to separate are often sanidine (or orthoclase) and biotite, and enrichment of Ba in these minerals has frequently been noted. It was observed that the bentonites in which barite was prominent showed little or no trace of sanidine and biotite. One of two explanations seemed the most probable. Either these two minerals, observed in other bentonites, had been destroyed with the liberation of Ba, due to pH and Eh conditions peculiar to these beds and unfavourable to the preservation of sanidine and/or biotite, or alternatively the ash had been formed from a Ba enriched magma, in which, possibly because of high temperature, the separation of the K-minerals had not begun. Subsequently, during the period of decomposition of the glassy ash in which the clay minerals were formed, Ba was liberated and, perhaps because of the prevailing Eh conditions, formed $BaSO_4$ in preference to going into the clay mineral lattices.

In an effort to determine the distribution of Ba in the bentonites, to find its relation to the occurrence of barite, and to throw further light on the nature of the original source materials, analyses of all the bentonites were carried out for this element. Furthermore, in view of the established substitution of Ba in the feldspar lattice, this mineral was also investigated, and the investigation extended to other sanidines separated for absolute age determination in this department.

The method adopted for the determination of Ba was that in which it is precipitated as $BaCrO_4$. A full description of this technique, the adaptations made, and the drawbacks to which it is subject, are given below. It will be noted that the method proved unsuitable for percentages of BaO less than .01.

The Method of Determination of Ba

Procedure:-

The usual method adopted for the determination of Ba is to precipitate it as $BaSO_4$. However, this has two important disadvantages. First, the precipitate is usually extremely fine-grained and is therefore difficult to filter quantitatively. Secondly, Sr is precipitated along with Ba. The method adopted, in which $BaCrO_4$ is precipitated, avoids both of these drawbacks. It is outlined below.

A one gram aliquot of the sample is fused with 5 grams of anhydrous Na_2CO_3 flux. (Where it is believed that the Ba concentration will be low, larger aliquots are used, and, if necessary, more than one fusion made). The cake is then broken up in water (most of the SiO_2 and some of the Al_2O_3 going into solution) and filtered. The filtrate is rejected and the residue on the filter paper dissolved by washing with 5% HCl. Some difficulty is experienced here if the SiO_2 has not been completely taken into solution, for it tends to clog the filter paper. In this case washing with more concentrated acid carries the SiO_2 through, and it is then removed along with the R_2O_3 precipitate.

The filtrate from this wash is brought to near the neutral point by adding a drop of methyl red indicator and a suitable amount of 50% NH_4OH solution. It is then heated to boiling and a normal R_2O_3 precipitation carried out. If a large sample has been used it may be necessary to carry out the filtration of this precipitate in two or more funnels, which can be set up at the same time to allow filtration while the solution is still hot. The precipitate is rejected. (No re-precipitation is necessary since it is of little importance, if anything to the good, that Ca and Mg will have gone in part into the precipitate).

The filtrate is usually rather large and is evaporated down on a steam bath to about 100 cc. and transferred to 150 ml. beaker. After it has been neutralized with a few drops of NH_4OH it is ready for the chromate precipitation.

0.05 ml. of glacial acetic acid and then 5 ml. of 25% ammonium acetate solution are added to the neutral solution to act as a buffer. It is then heated to boiling and a moderate excess of 10% ammonium (or potassium) chromate solution is added slowly. The solution is stirred constantly to encourage the growth of large crystals of $BaCrO_4$, and then allowed to stand for a day before being filtered on a 5 1/2 cm. blue band paper. A good deal of difficulty may be encountered in keeping the $BaCrO_4$, which creeps readily, in the filter paper, and if possible, the solution should be kept at all times well down in the paper. Finally, the precipitate is washed with 3% ammonium acetate solution until no trace of the chromate colour can be detected in the paper, and then twice more with cold H_2O.

The precipitate is ignited in a platinum crucible, fuming off the paper very slowly. The lid is then removed to keep the chromate fully oxidised, and the ignition completed. Green spots on the chromate indicate that it is partly reduced and it should be re-ignited until they disappear - if necessary with a

gentle jet of oxygen directed at the reduced areas. Ignition is carried out to constant weight.

Lead will be precipitated along with the $BaCrO_4$, but a fair separation from Sr can be achieved because of the relatively high solubility of $SrCrO_4$ (96 mg. $SrCrO_4$ in 100 g. of H_2O at 25°C.). Double precipitation can be carried out if an appreciable quantity of Sr is anticipated. The Pb concentration is usually very small and is ignored.

The main drawback to this method is that it is only suitable for determining relatively large Ba concentrations, and where these are not anticipated the sample weight has to be increased up to ten grams or more.

Investigation of the $BaCrO_4$ method for accuracy and sensitivity:-

Preliminary tests were carried out to determine the accuracy and limits of sensitivity of this method. A standard solution of $BaCl_2.2H_2O$ was made up, and $BaCrO_4$ precipitated as described above. Table (4) shows the results obtained.

TABLE (4)

No.	ml. of mg. BaO/ml soln.	BaO present in mg.	$BaCrO_4$ in mg. (found)	BaO in mg. (found)
1	1	1.00	1.4	.85
2	5	5.00	8.2	4.96
3	10	10.00	16.5	9.98
4	25	25.00	41.4	25.06

Only the smallest of the standards shows appreciable variation between the amount of BaO present and that detected, and this variation is of only slightly greater magnitude than the likely error in weighing. As a further check on the method a standard of pure $BaSO_4$ was carried through the same procedure as other samples - except of course that the R_2O_3 precipitation was omitted. Considerable discrepancies between the BaO expected and that detected, were found to be due to presence of adsorbed water in the finely powdered $BaSO_4$. When corrections had been made for this the results were directly comparable with those obtained in the first test.

It can be seen, then, that on a one gram sample one may expect to detect with a fair degree of accuracy down to 0.1% of BaO, and that quantities less than this will be apparent but not accurately determinable. In the case of the sanidine feldspars examined all gave measureable amounts of $BaCrO_4$ but, despite the fact that five and sometimes ten gram samples of the bentonite were used, in only one case was a weighable amount of the chromate precipitate obtained. This indicates that where ten gram samples of the bentonite were used certainly less than .005% BaO was present (and less than .01% where five grams were employed).

It is clear that this method is not suitable

for trace quantities of barium and indeed there seems to have been no reliable trace method developed as yet. The colorimetric method has little or no advantage over the gravimetric, since $BaCrO_4$ must first be precipitated as above, before being taken up in hydrochloric acid and determined on the colorimeter. However, for larger amounts of barium, and particularly in minerals and rocks where strontium is expected, the method is superior to that relying on the sulphate precipitation.

Results

TABLE (5) - BaO content of bentonites

Sample	Size of Sample	%BaO
Bentonite 3854-1	10 grams	(less than .005)
Bentonite 3854-2	5 grams	0.24
Bentonite 3854-3	5 grams	trace (about .01)
Bentonite 3854-4	5 grams	(less than .01)
Bentonite 3854-5	5 grams	(less than .01)
Bentonite 3854-6	10 grams	(less than .005)

Of the six bentonites analyzed only one, 3854-2, (0.24%) showed BaO present in weighable amounts. Thus the occurrence of barite in this bed must reflect high enrichment in the ash rather than peculiar conditions permitting its formation. A study of the mineral separates from this bed shows that apart from barite, apatite and quartz (showing the β habit), are the most abundant minerals. Both of these may crystallize

early and thus it seems probable that the molten material was ejected before appreciable quantities of the potassium-bearing minerals had started to form. (Some small contribution to the formation of barite may, however, have been made by the Ba in feldspars which have been largely replaced by carbonate. But the volume of this replaced material is very small compared to that of the whole rock). Further, the high enrichment in Ba indicates that the initial material was intermediate to acid in character, and that there had been no prior major period of crystallization of rocks bearing potassium minerals from this particular magma.

The comparative absence of Ba in the other bentonites must either indicate that they are formed from more basic differentiates not crystallizing potassium minerals, or from later differentiates deficient in Ba due to its earlier incorporation in potassium minerals.

The case in point serves to illustrate the usefulness of trace and minor element determinations in rocks such as bentonites, whose origin and initial nature are obscured by alteration of the modal character, and perhaps, major-element composition.

The conclusions regarding the late time of crystallization, or advanced position in the crystallization sequence, of the Number 6 bentonite, find further

support not only from the minerals present in the separates and the determined chemical composition, but also from the fact that the sanidine from this bed shows a relatively low Ba content.

TABLE (6) - BaO content of sanidine

Sanidine	X-ray	Chemical Determinations			
	% K_2O	Corrected % K_2O*	% Or Molecule	Corrected % BaO*	% Celsian Molecule
Crowsnest Volcanics	13.10	12.91	76.30	0.695	1.70
Millcreek Bentonite	12.52	11.34	67.01	0.135	0.33
Strawberry Ck. Bentonite	13.14	12.39	63.21	1.356	3.32
Bearpaw Bentonite	14.98	13.47	79.61	0.407	1.00
Exshaw Bentonite	12.16	12.77	75.48	0.121	0.30
Gaspe Bentonite	12.24	12.21	72.12	0.142	0.34
Kinnekulle Bentonite	12.69	12.08	71.38	0.499	1.22

* Corrections have been made to the %K_2O and %BaO determined by the tetraphenylboron and barium chromate precipitations, on the basis of the percentage of impurities in the separates. In the case of the Exshaw Sanidine, however, this is not possible. (See remarks under section on sanidines) and the values remain uncorrected.

Table (6), comparing the orthoclase molecule content of various sanidines, as suggested by the X-ray method of

Orville (1958) and as determined by chemical analysis (with correction made for contaminants), also shows the variation in BaO content. Quite clearly where this is high, the lattice dimensions of the crystals may be appreciably affected, and result in discrepancies between the K_2O content obtained by the two methods. It is also clear, however, that there is no simple relationship between the amount of the discrepancy and the amount of the Celsian molecule present. Other factors such as the An content, the temperature of crystallization and rate of cooling - in as much as it determines whether the high or low temperature state is preserved - might be expected to be of influence in this respect.

The variation in the BaO content of these feldspars can be taken to some extent as an indication of their time of crystallization relative to the evolution of the magma. The Strawberry Creek Sanidine, with over 1% BaO, indicates that it was amongst the first potassium minerals to crystallize from the magma, whilst the Gaspe Sanidine from the Number 6 bentonite, having less than 0.15% BaO, must have crystallized at a time when most of the barium had already entered into earlier potassium minerals. Thus, in general, the smaller the amount of BaO present in the sanidine the 'later' the rock in which it occurs. Of course the initial amount of barium in the magma will modify the

concentrations in various differentiates, and thereby the amounts in the sanidines, and the above criteria are only strictly applicable in a sequence of rocks that are clearly derived from one magma source.

Oftedal (1958) has found that the trends of the Ba (and Sr) values for eruptive rocks of the Oslo region support the geologically observed age relations. Also, the rocks of monzonitic and similar composition are comparatively rich in these elements, whereas the younger rocks become progressively poorer. He further notes that the absolute concentrations of Ba (and Sr) in the 'granites', as well as their coefficients of distribution between the feldspar phases of these rocks, seem to be rather insensitive to variations in the temperature of crystallization.

CLAY MINERALOGY

In view of the fact that clay minerals constitute a large proportion of the material present in bentonites a thorough examination of this component was undertaken by X-ray methods developed and described by Hendricks and Teller (1942), Bradley (1945, 1950, 1953), Brown and MacEwan (1950) and Weaver (1956, 1958).

Whereas mechanical mixtures of two clay mineral species always give rise to the two sets of reflections

characteristic of the species involved, randomly interstratified mixed layer clays produce one set of basal reflections which do not form an integral sequence. It is well known that the intensity of reflections from different clay mineral varies, and this factor becomes important in influencing the position of a maximum for a mixed layer clay. Thus three (10Å) illite layers interstratified with four (12.4Å) montmorillonite layers, will form a pile of 79.6Å thickness. Were it not for the difference in the scattering power of the two different types of layer (which is reflected in the different intensity of the corresponding peaks) the (007) peak for such a composite grain would lie at 11.37Å. In point of fact, randomly interstratified illite and montmorillonite in the ratio 3:4 produces a peak near 11.5Å. In an untreated interstratification of illite and montmorillonite, a further peak is produced by interference of 5.0Å (002) reflections (from illite) and 6.2Å (002) reflections (from montmorillonite) plus all reflections lying between 5.0Å and 6.2Å coming from composite grains with ratios of layers of the two clays other than 3:4. The position of the maximum is controlled by the overall average of the percentage of illite and montmorillonite present, and by the intensity of the various reflections. Weaver denotes such a peak as the (002)/(002) for the clay. A peak compounded from

the 5.0Å illite and 4.13Å montmorillonite reflections, plus those between from composite grains is then termed the (002)/(003) peak, and so on.

Theoretical curves can be computed for various proportions of illite and montmorillonite (or other interlayered clays) from the formula obtained by Hendricks and Teller (1942), and this has been done by Brown and MacEwan (1950), who have thus been able to graph the migration of the various peaks with changing amounts of the two clays. Weaver (1956) gives further information on this subject and illustrates his account with numerous diffractograms, with which comparisons can be made.

The interpretation of the patterns obtained from the Gaspe bentonites has been based largely on the data of Weaver (1956) and Brown and MacEwan (1950). The estimated clay mineral composition is shown in Table (7) below, the diffractograms are illustrated in Figs. 8 and 9 and the significant peaks are listed in Table (8).

The X-ray work on the clay minerals of the Gaspe material was carried out in this department on a "Norelco" X-ray diffraction unit and Minneapolis Honeywell recorder unit. Copper K_α radiation and a Ni filter, with standard voltage and current settings of 35 KV and 20 MA were employed throughout. The scale factor was varied to produce better peaks where necessary

but, in most cases, the setting 8-1-4 for scale factor-multiplier-time constant was found to give satisfactory patterns. In any case, the interpretation of the patterns obtained for mixed layer clays depends mainly on the position of the peaks, and differences in intensity (height) of the reflections will be introduced by variations in thickness, from one slide to another, of the clay mineral film. All the patterns were obtained using a recorder speed of 1/2 inch per minute and a diffractometer unit speed of 1/2 °2θ per minute and 2 °2θ per minute. It was found that somewhat better diffractograms, as regards the intensity and definition of the peaks, are obtained by reducing the recorder speed to 1/8 inch per minute and the diffraction unit speed to 1/8 °2θ and 1/2 °2θ per minute. This method was not, however, utilized as it means that each pattern takes four times as long to obtain, and it was considered that during this period of time a clay film might not remain fully glycolated. It is, however, desirable to have patterns for a particular clay treated in different ways (i.e. heat treated, glycolated and untreated), directly comparable. The diffractograms run at the faster speed of 2 °2θ per minute have been used for illustrative purposes, and determination of the position of peaks has been made from the patterns obtained at the slower speed. The slower speed runs allow greater

TABLE (7)

CLAY MINERAL COMPOSITION OF THE GASPE BENTONITES

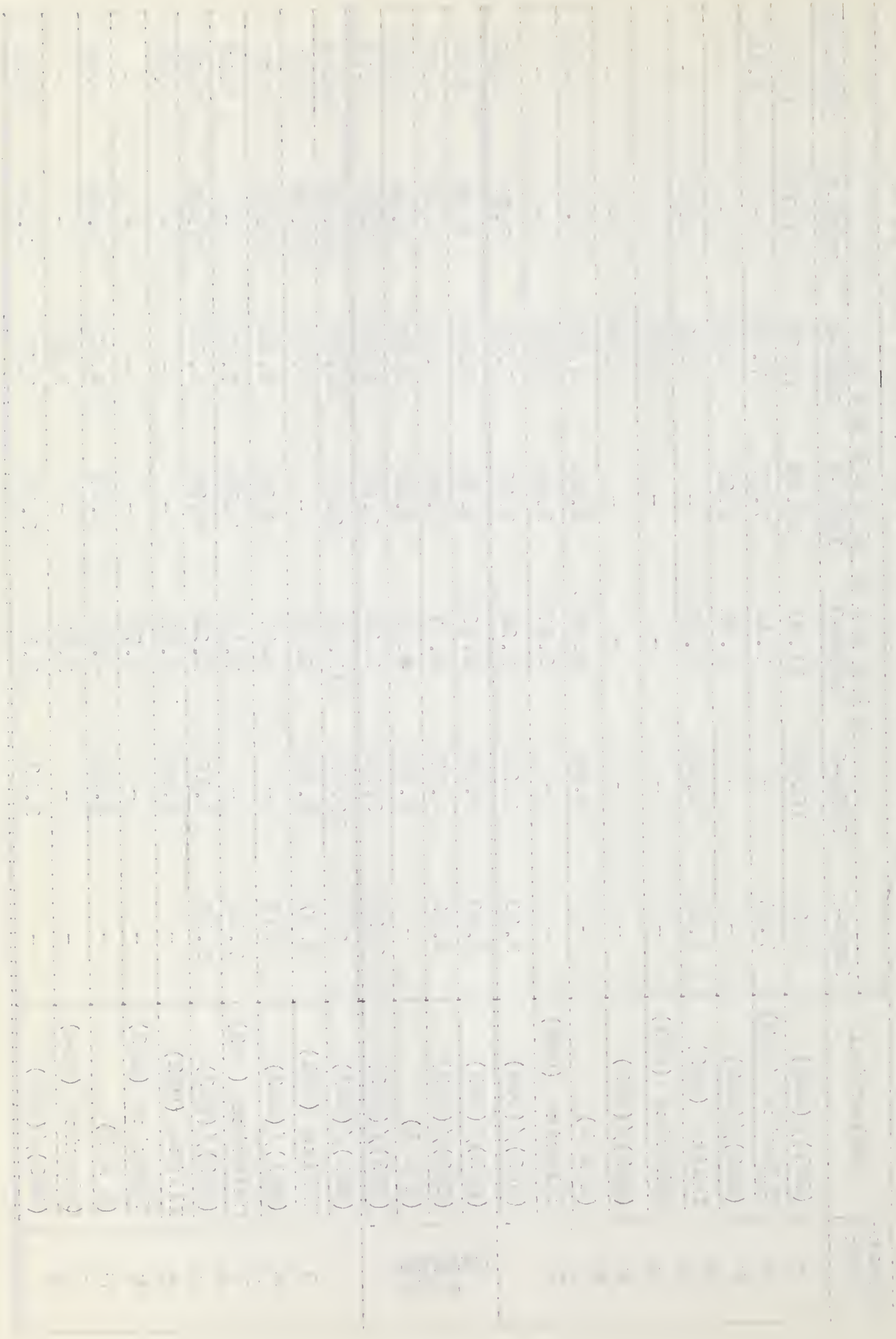
Sample No.	Illite	Chlorite	Montmor-illonite	Randomly inter-stratified illite and montmorillonite
3854-1	x	x	-	x (Illite:Montmorill-onite = 55.45)
3854-2	x	-	-	x (Illite:Montmorill-onite = 75:25)
3854-3	x	x	-	x (Illite:Montmorill-onite = 65:35)
3854-4	-	x	-	x (Illite:Montmorill-onite = 65:35)
3854-5	x	x	-	x (Illite:Montmorill-onite = 60:40)
3854-6	-	-	x	x (Illite:Montmorill-onite = 40:60)
3854-SP3	x	x	x	(Illite:Montmorill-onite = 60:40)

x denotes occurrence of mineral

- denotes absence of mineral

TABLE (8) - MAIN REFLECTIONS FOR THE GASPE CLAYS (Values given in Å)

Treatment	Reflection	Sample Numbers						
		3854-1	3854-2	3854-3	3854-4	3854-5	3854-6	3854-SP3
UNTREATED	(001)/(001)	11.21	10.48	11.01	10.99	11.31	11.78	11.18
	Chlorite (002)	7.17	-	7.15	7.17	7.17	-	7.15
	(002)/(002)	-	-	5.41	5.27	5.35	-	-
	Illite (002)	4.95	4.95	4.98	-	5.02	4.95	-
	Chlorite (003)	-	-	-	-	4.78	-	-
	(002)/(003)	-	-	-	-	4.69	-	-
	(h k l)	-	4.49	4.48	4.50	4.52	4.49	4.50
	Chlorite (004)	-	-	3.57	3.58	3.58	-	-
	(003)/(004)	3.23	3.24	3.24	3.23	3.23	3.23	3.23
HEAT TREATED	(001)/(001)	9.93	9.99	9.93	9.98	9.99	9.80	9.93
	(002)/(002)	4.92	4.97	4.97	4.96	4.94	4.89	4.92
	(h k l)	-	4.50	4.45	4.50	4.50	4.49	4.48
	(003)/(003)	3.28	3.30	3.29	3.29	3.29	3.26	3.28
GLYCOLATED	(001)/(001)	?	12.65	13.01	12.99	14.15	16.50	14.48
	Illite (001)	9.97	9.95	9.99	-	9.99	10.04	9.93
	(001)/(002)	9.17	-	9.27	9.35	9.40	8.98	9.22
	Chlorite (002)	7.19	-	7.15	7.17	7.17	-	7.17
	(002)/(003)	5.15	5.19	5.26	5.26	5.34	5.49	5.36
	Illite (002)	-	4.98	5.01	-	-	-	5.00
	Chlorite (003)	-	-	4.76	-	-	-	-
	(h k l)	-	4.50	4.50	4.49	4.52	4.48	4.50
	Chlorite (004)	-	-	3.57	-	3.58	-	-
	(003)/(005)	-	3.32	3.35	3.34	3.35	3.34	3.35



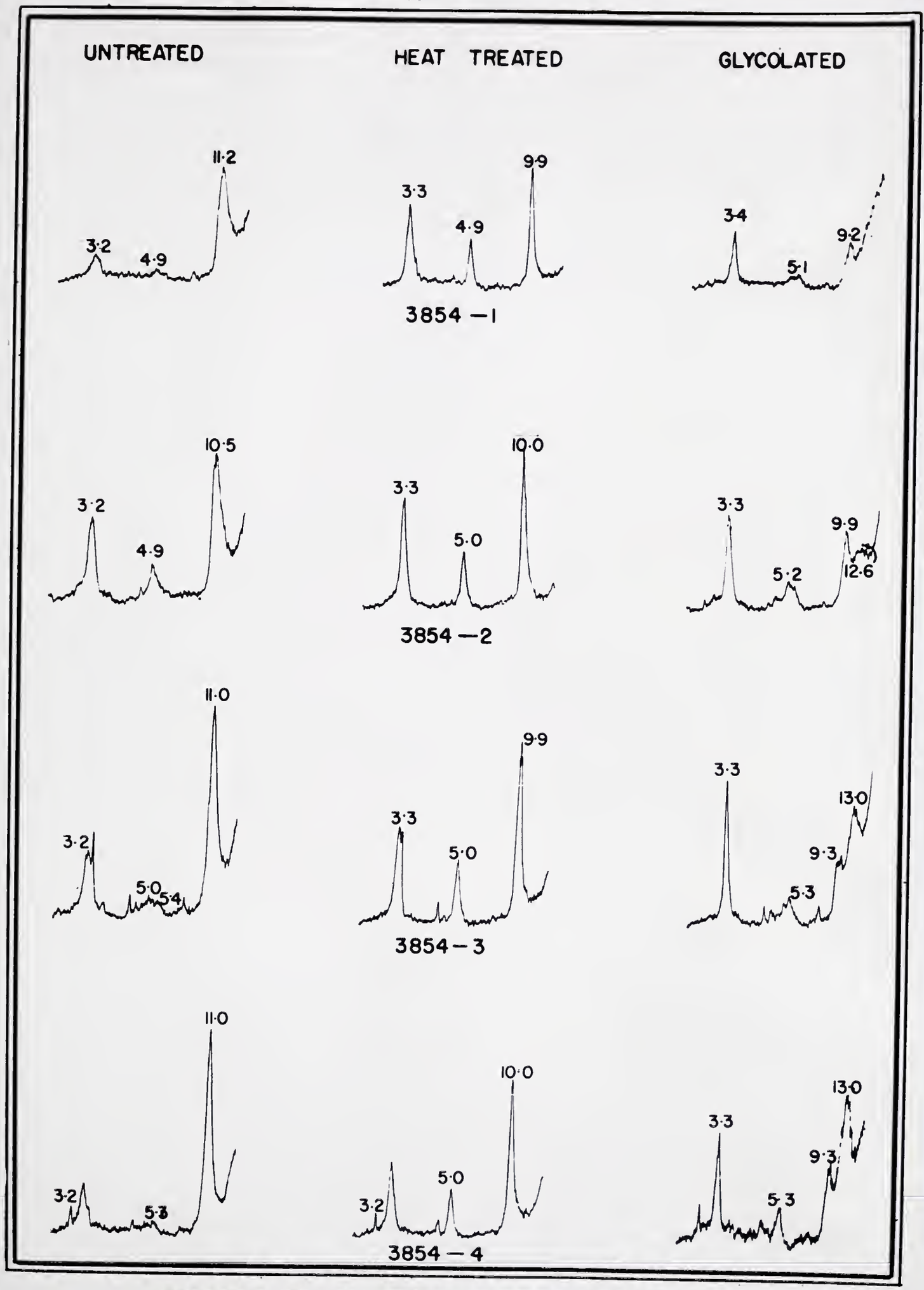


FIGURE: 8. 'X- RAY DIFFRACTOGRAMS.

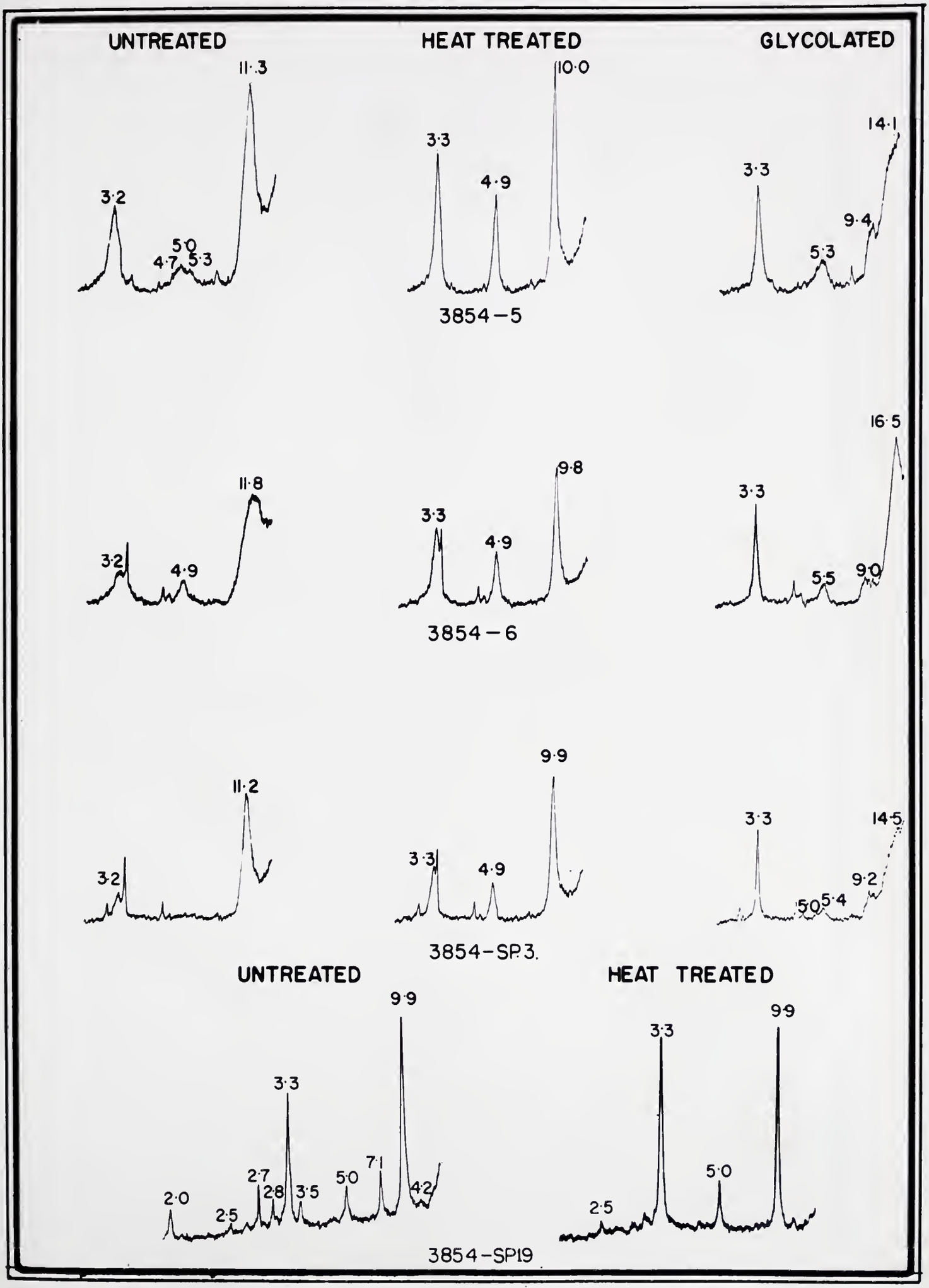


FIGURE : 9. X– RAY DIFFRACTOGRAMS .

accuracy in reading and in making any positional adjustments. The latter are based upon the deviation of one or other of the quartz peaks from the correct position.

One difficulty that was not overcome was the large build-up of background scatter at low angles. This means that the peaks for the larger first order spacings emerge from a, sometimes steeply, inclined base line. Where the d spacings are very large, as in glycolated montmorillonite, or when the intensity is small it is difficult, and sometimes impossible, to locate the precise position of a peak. (See for example the glycolated pattern for 3854-5, Fig. 9). This difficulty can be overcome by using narrower (1/4°) slits instead of the 1° slits normally employed. However these were not available in this department at the time the work was carried out.

SYSTEMATIC DESCRIPTIONS OF DIFFRACTOGRAMS:-

3854-1

Untreated clay:-

The (001)/(001) peak is rather broad, and the summit is split into two small peaks at 7.95°2θ and 7.75°2θ with an average peak at 7.89°2θ (11.21Å). This indicates a composition of about 45% montmorillonite and 55% illite layers (Weaver 1956). The (002)/(003)

peak is very broad and poorly defined, and the (003)/(004) peak is also broad, but the intensity is somewhat greater. Broad peaks are either an indication of varying percentages of expanded layers in the crystallites, or of a small number of unit layers in each crystallite.

There is evidence of the presence of chlorite from a (002) peak at 7.17Å, and illite could well be present, discretely, the reflections being masked by those from the mixed layer clay and/or quartz.

The main quartz peak is small and rather poorly defined.

Heat treated (15 minutes at 550°C.):-

The (001)/(001) peak has moved to 9.93Å as the montmorillonite layers collapsed. They are somewhat thinner than the illite (10Å), the precise thickness depending on the types and amounts of exchangeable cations present. The (002)/(002) peak, made up from the compounding of the second order illite and collapsed montmorillonite reflections now occupies more or less the position of the (002)/(003) peak in the untreated sample. However, the intensity in this case is quite high and the peak reasonably sharp. Similarly, the (003)/(005) reflection of the untreated sample is replaced by a (003)/(003) peak. It is much intensified and is close enough to the 3.34Å quartz peak to obliterate it.

The destruction of the 7.17Å reflection confirms the presence of chlorite.

Glycolated (for 48 hours):-

The (001)/(001) peak cannot be clearly identified as it is lost in the low angle scatter that results from the use of 1° slits. Possibly a peak exists at 16.2Å but equally several others can be found at smaller d spacings. No reliance therefore can be placed on the 16.2Å peak. Whilst there is a distinct and rather sharp peak at 9.97Å, another may be present at a somewhat smaller d spacing, largely camouflaged by the former. Its most likely position is at 9.17Å, but no great store can be placed by this figure. Probably the whole maximum results from the interference of (001) illite and (001)/(002) illite-montmorillonite reflections. Certainly if 45% of montmorillonite is present in the mixed layer clay, the (001)/(002) peak would be expected to move a good deal farther than 0.03Å from the 10.0Å pure illite position. The (002)/(003) peak at 5.15Å is also poorly defined and the (003)/(005) peak is indistinguishable from the main quartz reflection. However the asymmetry of the peak is taken to indicate that the 3.33Å/3.40Å reflection is approaching the 3.40Å position, thus confirming the presence of a considerable amount of montmorillonite. The (002) chlorite

peak at 7.19Å is clearly visible.

Conclusions with respect to 3854-1:-

The material is a mixed layer clay with about 45% montmorillonite and 55% illite layers randomly interstratified. There are also small amounts of illite and chlorite present, mixed mechanically with the other clay.

3854-2

Untreated clay:-

The (001)/(001) peak is asymmetrical and the correct position for the summit is difficult to determine with greater precision than $\pm$ 0.2Å. It is taken, however, as being 8.43°2θ which gives a d spacing of 10.48Å, indicating about 25% of expanded layers. No (002)/(002) peak is visible, but that at 4.95Å is probably the (002)/(003) peak. At 4.49Å is an (hkl) reflection common to all clay minerals. The (003)/(004) peak is quite large and at 3.28Å. (The 3.33Å/3.10Å peak decreases from a value of 3.31Å to 3.24Å as the percentage of expanded layers increases from 20% to 30%, but thereafter the decrease is less rapid). This figure confirms the previous indication of about 25% expanded layers being present.

No chlorite reflections are determinable and

neither are quartz and calcite apparently present. The asymmetry of the (001)/(001) peak may indicate the occurrence of some discrete illite.

Heat treated (15 minutes at 550°C.):-

All the reflections are considerably sharpened and the (001)/(001) peak at 9.99Å again indicates a relatively small amount of expandable layers. The "second order" of the compound peak is at 4.97Å. The (hkl) reflection is only slightly affected increasing .01Å to 4.50Å. The (003)/(003) peak at 3.30Å is much intensified compared with the (003)/(004) for the untreated clay.

Glycolated (for 48 hours):-

The (001)/(001) reflection is small and broad, further indicating a small amount of montmorillonite. The d spacing of 12.65Å is consistent with about 25% montmorillonite (Weaver 1956). The (001)/(002) peak is 9.95Å - only slightly removed from the 10.0Å illite position. The (002)/(003) maximum actually shows three peaks at 5.26Å, 5.12Å and 4.98Å. The 4.98 peak may well indicate the presence of some discrete illite (002) reflection) and the other two, which average at 5.19Å are probably a diffuse (002)/(003) reflection.

Conclusions with respect to 3854-2:-

This is a mixed layer clay, of composition 25% montmorillonite, 75% illite, which is mechanically mixed with some illite. Chlorite appears to be absent.

3854-3

Untreated clay:-

The (001)/(001) peak at 11.01Å is broad but quite sharp. The position indicates the presence of between 35% and 40% montmorillonite layers. There are broad and ill-defined peaks at 4.98Å (illite (002)), 4.48Å (hkl reflection), and 5.41Å ((002)/(002) for mixed layer clay). Weaver suggests that where three peaks can occur, one on either side of a central position, only the centre one shows up (Weaver, 1956, p.203-4), but this probably depends on the amount of the two components present. Thus when there is a high percentage of montmorillonite, say 80%, the (002)/(003) peak will approach 4.13Å and the (002)/(002), 6.2Å. These reflections will be quite widely separated, and a 5.0Å peak will be apparent only if discrete illite is present. If the reverse is true and 80% illite is present in the mixed layer structure, the (002)/(003) and (002)/(002) reflection will both be very close to the 5.0Å position and separated by a slight saddle only, which may well be lost in the background scatter. In this sample, because

of the presence of the 5.41Å reflection, it is believed that the 4.98Å peak is derived from discrete illite. Further, this general area of the pattern is complicated by the (003) reflection from chlorite, the presence of which is clearly indicated by a 7.15Å peak.

The (003)/(004) peak at 3.24Å is well removed and therefore quite distinct from the main quartz peak. The position of this reflection indicates at least 30% of montmorillonite layers. The quartz peak is much stronger than in the previous cases and the second quartz peak at 4.26Å is in this case clearly visible.

Heat treated (15 minutes at 550°C.):-

The (001)/(001) peak is sharp and at 9.93Å. The (002)/(002) peak is at 4.97Å and is slightly asymmetrical, which is taken to indicate that there is some discrete illite present producing a peak at or very near 5.0Å. Heating has moved the (hkl) peak slightly, to 4.45Å. The (003)/(003) peak is strong and at 3.29Å. The second order chlorite peak has been destroyed.

Glycolated (for 48 hours):-

Although still broad and rather diffuse, the (001)/(001) reflection is somewhat sharper than in the previous cases. It position at 13.01Å indicates that

just over 30% montmorillonite layers are present. The maximum between 9Å and 10Å is clearly made up of two peaks with d spacings of 9.99Å and 9.27Å. This is a comparable case to that obtaining in the glycolated pattern for 3854-1, and the fact that there is in this case a clear saddle between the two peaks, probably reflects only a smaller variation in the percentages of the two types of layer within the crystallite (or the larger number of unit layers present in the crystallite).

The (002)/(003) peak occurs at 5.26Å and a (002) illite peak at 5.01Å. There is a diffuse but definite (hkl) reflection at 4.50Å. The (003)/(005) peak coincides almost exactly with the 3.34Å quartz reflection, and the maximum is doubtless further complicated by the 3.33Å illite peak.

Chlorite peaks show up quite clearly at 7.15Å (002), 4.76Å (003), and 3.57Å (004). Whilst the (002) and (004) were visible in the untreated clay, the diffuse nature of the maximum between 4.5Å and 5.5Å obliterated the (003) reflection.

Conclusions with respect to 3854-3:-

The sample is made up of a mixed layer, illite-montmorillonite clay, which itself is mixed (mechanically) with a lesser amount of illite and a

small amount of chlorite. In the randomly inter-stratified mixed layer clay the proportions of illite and montmorillonite are indicated to be about 65% and 35% respectively.

3854-4

Untreated clay:-

The position of the (001)/(001) reflection at 10.99Å indicates a similar montmorillonite/illite ratio to that in 3854-3 - i.e. 35-40%. The (002)/(002) peak is at 5.27Å and is rather nearer the 5.0Å position than the corresponding peak for the previous sample. There is no indication of a 5.0Å illite peak in this sample, but the 4.5Å reflection is present as usual. The (003)/(004) peak at 3.24Å indicates at least 30% montmorillonite is present.

Chlorite is present as shown by 7.17Å and 3.58Å reflections, also carbonate (3.04Å), but quartz is noticeably absent.

Heat treated (15 minutes at 550°C.):-

The (001)/(001) peak at 9.98Å is in a slightly different position from the corresponding peak (at 9.93Å) in 3854-3. Since the collapsed thickness of the montmorillonite layers reflects the types and proportions of exchangeable cations present (thicknesses

vary from 9.4Å to 9.8Å in this way) a difference in these cations may well account for the variation noted. The (002)/(002) peak is quite sharp at 4.96Å and the (hkl) reflection at 4.5Å is present but rather diffuse. The (003)/(003) peak at 3.28Å is quite symmetrical due to the absence of quartz and probably of discrete illite. All chlorite peaks have been destroyed, but the carbonate reflection is again clear.

Glycolated (for 48 hours):-

Again the position of the (001)/(001) peak is very similar to that for 3854-3 (12.99Å instead of 13.01Å), further indicating about 30% expandable layers. Whilst a very small illite peak may be present around 10Å it is difficult to pick it out from the background, and the main reflection is at 9.35Å (cf. 9.27 in 3854-3). This is of course the (001)/(002) peak. The (002)/(003) peak occurs at 5.26Å and again there is no illite reflection at 5.0Å. The 4.49Å (hkl) peak is present but diffuse. The main quartz peak, if present, would be completely masked by the (003)/(005) reflection which occurs at 3.34, but this is absent as noted above.

Conclusions with respect to 3854-4:-

The sample is dominantly a mixed layer clay very similar in character to that seen in 3854-3, having

about 35% of montmorillonite randomly interstratified with 65% of illite. A little chlorite is mixed mechanically with this clay. Illite is noticeably absent, as is also quartz.

3854-5

Untreated clay:-

The position of the (001)/(001) reflection at 11.31Å indicates the presence of somewhat under 50% montmorillonite in the mixed layer clay. A (002)/(002) peak is apparent at 5.39Å, (002) (illite) at 5.02Å, (002)/(003) at 4.69Å, the (hkl) reflection. Furthermore, there is a suggestion of the (003) chlorite reflection at 4.78Å (the (002) reflection at 7.17Å is particularly sharp and clear in this clay sample). These five peaks together form one broad maximum.

The (004) chlorite reflection is quite strong at 3.58Å. Although the (003)/(004) peak is quite intense its summit is ill-defined. The best position is at 3.23Å - an indication that there must be somewhat more than 30% montmorillonite present.

The quartz peaks are quite weak and that at 3.34Å partially masked by the (003)/(005) reflection.

Heattreated (15 minutes at 550°C.):-

The (001)/(001) peak is at 9.97Å and is sharp

and intense. The (002)/(002) reflection at 4.94Å is also rather sharp. The main quartz peak is partly camouflaged by the (003)/(003) peak at 3.28Å. All the chlorite peaks have been destroyed.

Glycolated (for 48 hours):-

The (001)/(001) peak is indistinct but the position of the peak can be obtained by extrapolating the base line and replotting the peak. In this way a d spacing of 14.15Å is obtained, indicating just under 40% of montmorillonite layers. The (001)/(002) reflection at 9.40Å is consistent with this. There is a small but sharp (001) illite peak at 9.99Å and the chlorite (002) peak at 7.17Å is again relatively large and sharp. The (002)/(003) peak at 5.33Å is broad but quite distinct and is again consistent with about 40% of montmorillonite layers. The (002) illite reflection is not clearly visible but there is a hump on the side of the (002)/(003) peak at about 5.0Å. The (003)/(005) peak at 3.35Å completely obliterates the main quartz reflection, and the second quartz peak is not sharp enough to form a basis for correction.

The (004) chlorite reflection at 3.58 is sharp but the (003) is lost in the background.

Conclusions with respect to 3854-5:-

The sample is a mechanical mixture of a mixed layer illite-montmorillonite clay, and a little chlorite and illite. The mixed layer clay has about 40% montmorillonite and 60% illite layers.

3854-6

Untreated clay:-

This sample shows the broadest and most diffuse reflections of all the clays examined. The best position for the (001)/(001) peak is at 11.78Å, indicating the presence of about 55% montmorillonite. The (002)/(002) peak is not discernible (Weaver notes that this reflection is usually very weak) nor is the (002)/(003) peak. There is instead, a broad maximum in this general area with its summit at 4.95Å. Wherever the reflections are broad and diffuse these two reflections will be least likely to show up, and the broad build-up of energy in this area will be capped by the (002) illite reflection if that mineral is also present. The (hkl) reflection, at 4.49Å, is in evidence as usual.

The (003)/(004) peak at 3.23Å is also broad and diffuse. Its position indicates that there is something in excess of 30% montmorillonite (see comments under 3854-2).

The main quartz peak is strong and quite sharp, but the second quartz peak is rather poorly defined. Chlorite reflections are absent.

Heat treated (15 minutes at 550°C.):-

Heat treatment has moved the (001)/(001) peak to 9.80Å, suggesting either more montmorillonite layers than in most of the previous samples or else different exchangeable cations. The 4.89Å reflection is the (002)/(002) and the 3.26Å the (003)/(003) - and both of these give smaller values than those for the corresponding peaks of the other clays. Quartz peaks are quite distinct.

Glycolated (for 48 hours):-

The first peak is broad and diffuse. The best value for it, obtained by correcting for an assumed base line, and replotting, is 16.51Å. This would indicate the presence of about 70% montmorillonite. This figure may be too large, if there is also pure montmorillonite present forming a composite peak with the mixed layer clay reflection. The (001)/(002) reflection produces a rather small peak again indicating a large amount of interlayered montmorillonite, as does its position at 8.98Å. There is some indication of the presence of a small amount of discrete illite in a

barely discernible peak at 10.04Å. The (002)/(003) reflection again is broad and poorly defined. The best value for the summit, 5.49Å, is considerably larger than that for any of the other clays, further indicating a high montmorillonite content. No (002) illite reflection is apparent - but it may be present and lost in the background. The (hkl) reflection is present but weak. A small peak at 3.42Å is probably the (005) discrete montmorillonite reflection. The (003)/(005) peak is at 3.34Å, not as near the 3.40Å (pure montmorillonite) position as might be expected.

Conclusions with respect to 3854-6:-

The sample is a mechanical mixture of a randomly interstratified illite-montmorillonite mixed layer clay and montmorillonite (plus perhaps a little illite). Chlorite is absent. The ratio of illite to montmorillonite is about 40:60 - the lowest found in any of the seven samples examined.

3854-SP3

Untreated clay:-

(This sample, which is the clay fraction from the "bentonitic shale" above Number 5 bentonite, has been investigated along with the true bentonites for comparative purposes.)

A (001)/(001) peak at 11.18Å indicates about 45% montmorillonite layers are present in the mixed layer clay. The (002)/(002) and (002)/(003) reflections are lost in the background radiation and no 5.0Å illite peak is discernible. The (hkl) reflection is present, but very small. The (003)/(004) peak is broad and diffuse, but the best average value for it is at 3.23Å, indicating the presence of somewhat in excess of 30% montmorillonite.

Only one chlorite peak, at 7.15Å, can be determined, and this is rather weak. The first and second quartz peaks are quite strong and sharp and, unusually, a strong carbonate peak is also present (at 3.04Å).

Heat treated (15 minutes at 550°C.):-

A (001)/(001) peak at 9.93Å indicates again a fair proportion of collapsible montmorillonite layers. The (002)/(002) peak at 4.92Å is quite strong, but the (hkl) reflection at 4.48Å is just discernible, as in the untreated material. The (003)/(003) peak occurs at 3.28Å and a minor peak lying between it and the main quartz peak, may be the (003) illite. The one chlorite peak visible in the untreated clay has been destroyed.

Glycolated (for 48 hours):-

This pattern suggests that discrete montmorillonite may be present as well as that in the mixed layer clay. A peak appears at 17Å, and then the (001)/(001) peak may be anywhere between this peak and the saddle at about 10.5Å. Extrapolation of the base line curve and correction for this suggests a peak at about 14.5Å, but no great reliance can be placed on this value, although it is consistent with there being about 40% of interlayered montmorillonite present. The reflection around 10Å is again very poorly defined although it does appear to be composite and made up of the (001) illite reflection and the (001)/(002) reflection at about 9.22Å. Neither peak is sharp and therefore neither can be read with much accuracy. Again, however, 9.22Å is consistent with 40% of montmorillonite layers. There is a very broad (002)/(003) peak at 5.36Å and a very weak (002) illite reflection at 5.00Å. The (hkl) reflection at 4.50Å is present but small. The (003)/(005) reflection completely masks the quartz reflection (or vice versa) but the symmetry of the peak indicates that the former lies at 3.35Å.

As in the untreated material only the (002) chlorite reflection is apparent.

Conclusions with respect to 3854-SP3:-

This sample is a mechanical mixture of a randomly interstratified mixed layer illite-montmorillonite clay with a little chlorite, illite and montmorillonite. The proportions of illite and montmorillonite are about 60% and 40% respectively. The sample differs in no major aspect from the clays obtained from the bentonites.

3854-SP19

The sample is the green-coloured matrix from the "grass-green" bed at the top of the Shiphead Member. As mentioned in the chapter on stratigraphy, it had previously been identified as chlorite. However, the X-ray examination detailed below clearly indicates that it is a mechanical mixture of glauconite and chlorite with the former dominant. Two diffractograms, one for the untreated, and the other for the heat treated material are shown in Fig. 9. Heat treatment has destroyed the chlorite peaks but left the glauconite peaks unaffected. The sharpness of the glauconite peaks and the indicated basal spacing of 9.95Å show that this is a well ordered glauconite (Burst, 1958). Quartz and calcite peaks are also present (see also Fig. 7).

Reflection	Untreated 'd'	Heat Treated 'd'	Glycolated 'd'
Chlorite (001)	14.20	-------	14.24
Glauconite (001)	9.95	9.95	9.94
Chlorite (002)	7.13	-------	7.13
Glauconite (002)	4.97	4.97	4.97
Chlorite (003)	3.55	-------	3.54
Glauconite (003), (022)	3.31	3.31	3.31
Glauconite ($11\bar{3}$)	2.82	-------	-------
Glauconite (023)	2.66	-------	2.66
Glauconite (004)	2.49	2.49	2.48
Glauconite (005)	1.98	-------	-------

TABLE (9)

REFLECTIONS FROM 3854-SP19

General discussion of results and conclusions

All the samples examined (except 3854-SP19) are basically similar, being mechanical mixtures of randomly interstratified illite-montmorillonite, with lesser amounts of chlorite, illite and, in one case at least, montmorillonite. However, it is quite impossible to determine quantitatively the proportions of the three or four components of these clays. Even when two clays (say

illite and montmorillonite) are present alone, and mixed mechanically, estimates of their proportions made by comparing the areas under the respective peaks are only good to about 10%. Differing degree of crystallinity contributes to the margin of uncertainty, as does background radiation. In the case where mixed layer clays are present, many further complications are added. Broad peaks may result from the fact that, in particular grains, the percentages of component illite and montmorillonite layers depart widely from the average, or that the crystallites contain few unit layers, i.e., they are largely made up of several layers of one species interleaved with several layers of the other (mering 1949). Poor sedimentation during preparation results in a further broadening of the peaks. Thus, any attempt to give more than a general idea of the proportions of the components, in these cases, would be hazardous.

It will furthermore be noticed that there is not always complete agreement as to the proportions of the interlayered clay species when calculated by the positions of different reflections. Weaver (1956) remarks "In some cases the ratios of layers determined from the 10/12.4-Å curve and the 10/17-Å do not show exact agreement. In most cases this discrepancy may be caused by the presence of a few intergrown chlorite layers,

as the measured 10/12.4-Å value is usually too high and the 10/17-Å value too low. Heat treatment indicates that the chlorite layers are relatively scarce." This explanation seems quite acceptable in the case of the Gaspe clays where discrete chlorite is present in most cases. Where such a discrepancy arises the average value has been taken.

Finally, it is not certain to what extent the occurrence of discrete illite and montmorillonite results from the breaking down during preparatory treatment of the composite grains. Where such grains are made up of packets of illite and montmorillonite sheets (as is perhaps indicated for the Gaspe clays by the broadness of the peaks) this effect may well be considerable.

Until the recent tremendous expansion in the investigation of clay minerals, which has come with the development of D.T.A., X-ray and other new techniques, it was popularly believed that bentonites were characterised by the clay mineral montmorillonite. Thus Ross and Shannon (1926) proposed that "Bentonite is a rock composed essentially of a clay-like mineral formed by the devitrification and accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash." However, they go on to add " .... the characteristic clay mineral is montmorillonite." A

brief survey of recent literature on the clay mineral content of volcanic ash beds and "bentonites" soon reveals that such beds bearing montmorillonite alone are the exception rather than the rule (see for example Birrel and Fieldes (1952), Gradwell and Birrell (1954), Gordon et al (1955), Byström (1956), Weaver (1953), Orr (1959)). Adhering strictly to the definition given above, such beds should not be termed bentonites, but it is held that the limitation of the term to the cases where montmorillonite is the only clay mineral species present is, in the light of present knowledge, arbitrary and unnecessary. As used in this thesis the term has the meaning given by the first part of Ross and Shannon's definition.

In the light of these reports the composition of the Gaspe bentonite clays is not considered particularly unusual. Indeed there are many similarities with the clay fractions of the Ordovician Medonte bentonites described by Orr (1959) and with those from Kinnekulle, dealt with very thoroughly by Byström (1956).

To what extent the present chemical composition of a bentonite reflects the initial composition of the ash, and to what extent it reflects the chemistry of the environment into which it was suddenly transported, is a problem that still remains largely unsolved. Many workers have postulated chemical alteration either by

direct contact with sea water soon after deposition, or subsequently by base exchange between percolating solutions and the ash. In the first case, for example, if the ash falls into a marine environment with a high concentration of calcium ions, montmorillonite will be formed by the leaching of potassium and enrichment in calcium. Subsequently, this clay might be modified by exchange with percolating potassium-bearing solutions to a mixed illite-montmorillonite clay.

It may be, however, that too much emphasis has been laid on the chemical alteration of bentonites, possibly because of their almost complete mineralogical alteration. Whilst it may reasonably be assumed that the glassy ash will be quite out of equilibrium with its new environment, and, being of a finely powdered and poorly crystallized nature very susceptible to alteration, it must also be remembered that ash beds are often (initially) thick and rapidly deposited so that reaction with sea water will be considerably hampered. Furthermore, any exchange of cations should become of significance only after the devitrification of the glass has allowed the formation of the basic clay mineral lattices. By the time this point is reached it is quite probable that the bed will be fairly deeply buried by superincumbent strata and thus out of direct contact with the water in which it was laid down.

There is also the possibility that chemical changes are brought about by percolating solutions. Although the ash is initially very porous, with the development of clay minerals, particularly the hydrated species, pore spaces will be taken up by increase in volume of the material. At the same time compaction will take place by the normal load process. The final product is a compact rock with a waxy appearance and conchoidal fracture (for some reason, probably to be sought in the fact that the clay minerals are not detrital, but formed in situ, bentonites do not seem to readily acquire the degree of fissility imparted to other mudrocks - even those in the same sequence). The present writer believes that it is during this stage of compaction that most of the chemical alteration takes place, and that it is mainly limited to hydration, together with minor additions of cations such as Ca^{++} and Na^{+}, and possibly the leaching of others such as K^{+}. Silica may also be leached to a small extent at the same time. Subsequent to this it seems unlikely that chemical changes will be very great. Recently, Weaver (1958), in presenting his controversial views on the "Geologic interpretation of argillaceous sediments", has cast serious doubt on the view, until then widely held, that diagenetic changes in clays are widespread and often in operation long after the deposition of the clay. Instead,

he suggests that what has been termed diagenesis is better referred to as cation adsorption, and that most clay minerals strongly reflect the character of the source material, being modified only slightly in their depositional environment. He later points out that "montmorillonite deposits formed from one volcanic source are strikingly uniform in composition; however, montmorillonites formed from volcanic material from different sources are usually quite different in composition."

Finally, there remains the possibility that reworking of an ash fall may take place and thus increase the likelihood of reaction between it and the water in which it is deposited. It is believed that some, at least, of the Gaspe bentonites have suffered a certain amount of reworking, for in several cases the upper layers, and sometimes lower horizons, are traversed by small animal burrows. Furthermore, the upper portion often becomes shaly in character, developing a fissility more or less absent in the main body of the deposit. It is believed that the main source of contaminating detrital minerals, noted in heavy mineral separates is to be found in these layers; also, that the 'bentonitic shales' occurring throughout the sequence result largely from the reworking of ash falls - either within the depositional basin or from the adjoining land

mass. In the case of 3854-SP3, the bentonitic shale that was examined along with the other clays, it will be noted that the illite:montmorillonite ratio is not strikingly different from that in the other samples. This suggests that in this case reworking has had little effect in changing the composition of the clay.

With regard to the environment in which the clays were deposited, the interbedded limestones with their marine faunal assemblage, the presence of some beds with plant remains, the occurrence of glauconite in the upper zone, together suggest that this was an area of shallow seas, into which little detrital material was carried - except perhaps after the periodic volcanic eruptions. The presence of limestones above and below the bentonites indicates that the pH must have been above 7.8.

CONCLUSIONS FROM PETROLOGICAL STUDY

PRESENT COMPOSITION:-

All the bentonites are now composed dominantly of clay minerals with a lesser amount of quartzo-feldspathic aggregates. Minor amounts of holocrystalline material are however invariably present, although some of this is of authigenic origin. Amongst the heavy minerals, apatite, zircon, barite and pyrite appear consistently, while biotite, garnet, spinel and rutile have a more restricted occurrence. Quartz dominates the light minerals but most of the bentonites have some feldspar in the form of sanidine and/or plagioclase.

SOURCE MATERIAL:-

The presence of one or more of quartz, sanidine, sodic plagioclase, and quartzo-feldspathic aggregates suggests rhyolitic or trachytic affinities for the original source material. This conclusion finds some support in the case of 3854-6, from the total chemical analysis. Furthermore, the Ba determination in conjunction with the composition of the sand fractions, indicates that, with the exception of 3854-2, the source material formed subsequent to the phase of Ba enrichment which normally takes place in the intermediate stages of differentiation, when the first potassium minerals separate.

DIAGENESIS:-

Clearly the main change that has taken place in the rock since its deposition as an ash is the devitrification of the aphanitic material and its subsequent, probably penecontemporaneous, conversion to clay minerals. The composition of the clay material has probably been altered somewhat during the early stages of diagenesis by cation exchanges.

At least two heavy minerals, barite and pyrite, have developed authigenically. The former is believed to have formed at about the same time as the clay minerals since the Ba would be expected to be liberated from the glass at the time of its decomposition. The presence of pyrite alongside the barite is somewhat enigmatic since the two minerals are indicative of different Eh conditions, forming on opposite sides of Krumbein and Garrel's (1952) sulphate-sulphide 'fence'. Possibly the pyrite formed earlier by the action of reducing bacteria on organic material (evidence of which is found in most of the bentonites in the form of sponge spicules, spores or ostracods - the first and second of these have been observed to actually be infilled with pyrite). Later, more oxidising conditions would have permitted the formation of $BaSO_4$, possibly at the expense of some of the pyrite. However, the conditions cannot have changed radically, since much of

the pyrite persisted unaffected.

Apatite is generally considered to be unstable in an acid environment and its occurrence in all of the bentonites can be taken to indicate that the pH within the beds was never very low. Furthermore, as has already been noted, in some cases authigenic overgrowths are visible and the formation of a mineral, as distinct from its persistence, is a sure indication of a favourable environment. It seems likely that the phosphate required for the growth of the mineral, like the Ba for barite, was liberated by the breakdown of the volcanic glass.

The etching of garnet is held by some writers to indicate acid conditions, whilst others believe the opposite is true, and that basic conditions produce this effect. As yet, it seems that no firm conclusions can be drawn on the subject.

Finally, the formation of montmorillonite, because of the low Al:Si ratio in the mineral, is generally believed to be favoured by neutral to slightly alkaline conditions (Mason, 1958, p.154).

The balance of evidence thus indicates that the conditions in the bed, at the time when the important mineral changes were taking place, were slightly alkaline and reducing with a pH of about 8 and Eh of -0.2 to -0.3.

ENVIRONMENT OF DEPOSITION:-

There is no reason to assume that the Eh-pH conditions deduced above, can be extended to the environment in which the ash was deposited. However, since fine grained, possibly chemically precipitated, limestones were deposited in the intervals between bentonites, it is probable that the ash fell into slightly alkaline waters.

The general character of the Shiphead sequence with the succession of fine grained fossiliferous, argillaceous limestones and shales, the occasional arenaceous bed, and, at the top of the Forillon Member, biohermal limestone, suggests a fairly shallow marine environment into which only the finest silt and clay grade material was being transported. The latter may reflect either the fact that the surrounding landmass had little relief, or that the area of deposition was at some distance from the shore line. The shallow nature of the seas is also indicated by the presence of plant remains in the Shiphead strata, and by the uneven surfaces found at the top of some of the bentonites (e.g. 3854-4, Fig. 5).

CONTAMINATION:-

It is believed that the bentonites contain only a very small amount of detrital material of non-

volcanic origin, for the following reasons:-

(i) The sanidine separates do not show any evidence of contamination by the other potash feldspars, microcline and orthoclase.

(ii) The mineral suites obtained from the beds are always relatively simple.

(iii) Certain euhedra, notably of apatite and zircon, that are obviously of volcanic origin completely dominate rounded grains. The latter in the case of zircon may anyway result from magmatic corrosion.

(iv) The ash falls, in terms of geological time units, are deposited more or less instantaneously, allowing no time for an influx of significant quantities of extraneous material.

However, contamination can result from the pulverising and admixing of large amounts of the country rock at the time of the eruption, from the reworking of the upper layers of the bentonite by burrowing creatures, and by the direct incorporation of organic matter at the time of deposition. All these factors can be observed in one or other of the Gaspe bentonites. 3854-1 contains a significant amount of chromite which is obviously not cogenetic with the quartz and sanidine present, but which, it is believed, may come from the incorporation of ultra basic material at the time of the volcanic explosion. The same bed has a microfauna and microflora of ostracods,

sponge spicules and megaspores. Most of the bentonites contain traces of burrowing animals in their uppermost layers, and sometimes in lower horizons (which can be taken to indicate that the bed formed from more than one eruption).

Any contamination resulting from reworking can be avoided by sampling only layers that show no traces of animal burrows. Organic matter is of no consequence as far as absolute dating purposes are concerned except in that chalcedonic sponge spicules are extremely difficult to eliminate from the feldspar separates. Finally, the significance of contamination from pulverised country rock can only be assessed by a thorough study of the mineral separates from the bed, whereby the nature of the contaminant may be determined.

PROVENANCE:-

No definite conclusions can be drawn as to the source area of the Gaspe ash falls. Several localities are known in, or adjacent to, the Gaspe Peninsula where Devonian igneous rocks occur - such as that around Dalhousie, N.B., or the central Gaspe region (see Fig. 1). However, the source could well remain as yet undiscovered or unexposed.

A B S O L U T E D A T I N G

GENERAL STATEMENT

The preliminary investigations of Folinsbee referred to earlier, had shown that the desired potassium minerals were not present in abundance in the Gaspe material. Accordingly, a careful and systematic examination of all the separates was carried out to determine which bentonites had small quantities of biotite, sanidine and zircon, and whether there was sufficient present in 100 lb. samples of the raw material for reliable dating work to be carried out.

The occurrence of sanidine in several of the bentonites was revealed, but in only two, Numbers 1 and 6, was it present in sufficiently large amounts. In addition, biotite and zircon were present in both of these beds. Of the two, the Number 6 was chosen because of the 'cleaner' appearance of the sanidine separate (albite is present along with the potash feldspar in Number 1), and the less chloritized nature of the biotite. Furthermore, the Number 1 bed showed a particularly large concentration of sponge spicules, and these, having approximately the same specific gravity and magnetic properties as sanidine, are extremely hard to separate from it.

SEPARATION TECHNIQUES

The raw bentonite was put through a jaw crusher several times until all the grains passed through a U.S. number 35 mesh sieve. This semi-disaggregated material was then placed in water in a 2 litre beaker where it was allowed to remain soaking for two days to separate clay and silt grades from sand. The latter fraction was finally recovered by decanting the silt and clay into a large bottle, and was then dried.

Sieving of the sand fraction was carried out in the normal way using a 15-minute period on a Ro-Tap machine. The U.S. sieve intervals 80, 120, 170, 270, and 325 were used. Prior examination of the sand fractions from the bentonites, small amounts of which had already been treated in the course of Folinsbee's earlier work, revealed not only which bentonites contain the desired potassium minerals, but also the size fraction in which these are concentrated. For example, it was apparent that sizes +120 mesh contained little, if any, of these minerals. It was thus possible to select the uppermost bentonite and the -120 fractions as being most fruitful.

Accordingly, each fraction was run through a Frantz magnetic separator in turn, and a number of different field strengths applied to obtain concentrates

of the biotite and sanidine. First, a setting of 0.2A slope 18°, tilt 8° was found to remove very magnetic iron-rich material, whilst not pulling over the biotite. A setting of 0.4A, slope 18°, tilt 8° would remove the biotite quantitatively in the -120 +170, -170 +270 fractions, although it was necessary to repeat the operation several times for maximum recovery in the finer fractions. A further setting of 1.7A, slope 18°, tilt 8°. removed the bulk of the remaining material leaving the sanidine concentrated in the 'non-magnetic' pan. Repetition of this last operation eliminated a good deal more of the unwanted matrix. At this point the tilt was progressively decreased one degree with each re-run until a tilt of 1° had been reached and the sanidine thus greatly concentrated. It was found most satisfactory to proceed in the above manner, for, if a tilt of 1° wasused in the first instance, the great bulk of material pulled over onto the magnetic side of the instrument would carry much of the sanidine with it and this would necessitate the continual recycling of a large quantity of material.

The concentrate of non-magnetics was then ready for heavy liquid treatment. A number of separations of this kind were carried out as follows:-

(1) Pure tetrabromoethane, S.G. 2.96, was used to separate 'heavies' from 'lights'.

(2) Tetrabromoethane and acetone, S.G. $\sim$ 2.55 to separate quartz, plagioclase feldspar, etc., from sanidine.

(3) Tetrabromoethane and acetone S.G. $\sim$ 2.45 to separate feldspar from lighter material (mainly matrix and sponge spicules, but also any glass fragments that might have been introduced at a previous stage).

(4) Tetrabromoethane and acetone, S.G. $\sim$ 2.75 to separate biotite from any lighter materials of similar magnetic properties.

The specific gravities of the liquids used in (2) and (3) were adjusted by adding acetone to the tetrabromoethane, until, in the first case quartz sand and sanidine feldspar just floated, and in the second feldspar just sank. In this respect it is worth noting that a considerable variation was observed in the specific gravity of the sanidine phenocrysts used for this test purpose and one had to be selected by trial and error to correspond as closely as possible to that of the Gaspe sanidine. (The amount of the Celsian molecule present in a feldspar is important in influencing the specific gravity). In the case of (4) the specific gravity was adjusted until quartz just floated. Because of the small size of the concentrates it was worthwhile and time-saving to use a centrifuge in all heavy liquid separations.

The biotite and sanidine fractions were then returned to the magnetic separator. The former was run

through the instrument two or three times to obtain as pure a separate as possible. The sanidine, however, was recycled between twenty and thirty times, in the later stages reducing the tilt to 1/2°, to remove as much as possible of the remaining contaminants (which at this stage consisted mainly of quartzo-feldspathic aggregates). Because of the very small amounts involved, it was necessary here to repeat this process at least twice on the material which had been rejected, and which contained as much as 30% sanidine. In this way, 90% or more of the sanidine was eventually recovered. However, even after this drastic treatment, the final purity of the coarsest sample was only about 70%, and of the finer fractions, somewhat less.

Zircon, because of its higher specific gravity, is concentrated in even finer fractions than the sandine, that is, -270 +325 and -325 (pan). This effect is no doubt enhanced by the slender needle-like habit of the crystals which permits them to pass through the finest of sieves. The only satisfactory way to recover this mineral from the -325 fraction is by the process of simple panning, whereby the finest and lighter material is washed off leaving the residue enriched in zircon. From this point onwards, normal procedures of magnetic and heavy liquid separations are adopted as follows. Zircon, being only very slightly magnetic, is concentrated

in the non-magnetic fraction even down to a current setting of 1.7A. However, settings greater than 1.2A result in some of the zircon being drawn into the magnetic pan, and the best concentration is obtained by recycling the material at 1.2A until a sufficiently small volume for heavy liquid separation is obtained (this point is usually reached quite rapidly). If the volume of the zircon concentrate is small, the subsequent separation may be carried out directly in methylene iodide (S.G. 3.3). If it is large, a preliminary separation in pure tetrabromoethane (S.G. 2.96) is advisable since this procedure minimises the size of methylene iodide washings.

If pyrite is found to be present in the zircon separates (it often is) the next step is to roast the material for five minutes at 500°C. This treatment oxidises the pyrite to a magnetic form, but apparently has no ill effects on the zircon. The separate is then purified on the magnetic separator, the field strength being increased until a significant amount of zircon begins to be drawn into the magnetic fraction. The only contaminants encountered by the writer by the time this stage was reached was barite. No satisfactory method of separating the two quantitatively was found, but concentration could be effected by drawing the zircon into the magnetic side and leaving

most of the non-magnetic barite behind. Recourse could perhaps be made to Clerici's solution (Clerici, 1907, 1922; Vassar, 1925) but this is extremely difficult, and somewhat dangerous, to work with, and even then the specific gravities of zircon (4.7) and barite (4.8) are so close that quantitative separation is unlikely to be achieved, particularly in the finest grain size. Tilton (in personal communications to Folinsbee) has indicated that differential crushing of the more brittle barite can be used to rid a sample of this unwanted mineral. Otherwise an estimate of the impurities can be made by counting.

Three separates of sanidine (-120 +270 mesh, -270 +325 mesh, and -325 mesh) and two of biotite (+270 mesh and -270 mesh) were obtained. Despite long and painstaking efforts to purify the sanidine, all of the separates of that mineral were more or less contaminated with quartzo-feldspathic aggregates, quartz and sponge spicules, and very minor amounts of plagioclase feldspar. These impurities are reflected in the K_2O content of the sample, which drops with decreasing grain size. This is because quantitative separation of minerals of similar specific gravity below 270 mesh is very difficult when high recovery is vital. Only the quartzo-feldspathic aggregates, which are considered to be rapidly and poorly crystallized, are likely to

contribute to the potash content, and then only in relatively small amount (see appendix, p.156). The biotite separates were obtained under similar difficulties but the higher specific gravity and very magnetic character is shared by a much smaller amount of material than is the case for sanidine, and much purer separates were obtained, the material giving the most trouble in this case being grains rich in iron oxide.

THE K/Ar METHOD OF ABSOLUTE DATING

This recently developed method of absolute dating depends upon the radioactive decay of K^{40} by K-electron capture to Ar^{40}. K^{40} also decays by β-particle emission to Ca^{40} and the two-fold nature of the decay introduces what at present remains one of the major drawbacks to the method. Despite many measurements of the disintegration constant for β emission, by various methods, there still remains an uncertainty of about 10% in the figure now in use. However, it must be emphasised that inaccuracies introduced in this way are the same for all results, and do not affect the relative values. When more precise counting data become available, therefore, any necessary correction can be readily applied to all K/Ar results.

Whilst it is not proposed here to describe at great lengths the details and techniques of argon liberation, purification and measurement, a brief description of the method follows.

A carefully weighed amount of the sample is suspended in a glass vial in the argon train which is afterwards closed to air and evacuated. The sample is then dropped into a nickel crucible in which fusion takes place (NaOH flux heated to 700° is used), and the argon and other gases (mainly water vapour) are liberated. At this point the 'spike' argon is introduced to mix with these gases, which are drawn to another part of the train (by adsorbing them on charcoal cooled to liquid air temperature) for purification. Water vapour is removed by use of $Mg(ClO_4)_2$ and 'cold' traps, hydrogen with copper oxide, and then the final cleansing is carried out by means of a uranium getter. The only gases contaminating the argon at this stage should be other inert gases. The advantage of this, the isotope dilution method, over the original 'absolute volume method' is that a small amount of these impurities do not matter, for the final calculations are based only on the changes in ratios of argon isotopes from those initially present in the 'spike' argon.

The purified sample is re-trapped on charcoal at liquid air temperature and sealed off ready for mass

spectrometric isotope ratio analysis. A photograph of the argon train is shown in Fig. (10).

The mass spectrometer, set up by J. Lipson in the Physics Department at the University of Alberta is a Nier type, six-inch, 60° instrument, with a metal tube, incorporating Reynolds electronic circuitry. Upon its efficient operation the successful dating of a mineral is very much dependant.

A typical example of the recording obtained from the mass spectrometer chart, on which all subsequent calculations are based, has been reproduced by faithful tracing in Fig. (11). The curves showing the pressure-volume decay of the Ar^{40}, Ar^{38} and Ar^{36} peaks can either be drawn directly through the tops of the peaks (or somewhat below, where an adjustment has to be made for base-line variation), or can be plotted from readings printed by a digital voltmeter. Usually there is little or no discrepancy in the result obtained by the two methods, but the latter is preferable when the tops of the peaks are sharp (i.e. not flat-topped) or unstable, as the rate of printing can be increased to give a better average. Other lines shown on the chart are the Ar^{40}, Ar^{38} and Ar^{36} residuals which result from desorption from the walls of the instrument, and/or minute leaks. Corrections are obtained for these from a dummy run in which the build-up of these peaks with time

is found and the results are applied to the later run on the argon liberated from the specimen.

One further measurement is made on the mass spectrometer, this being of the ratios of Ar isotopes in air. For this purpose, commercially purified Ar, obtained from air, is used. Assuming that there has been no isotope fractionation during the concentration of the gas, the ratios should be the same as those obtained for air (Nier, 1950). The fact that there is a slight discrepancy in the two sets of values indicates a minor discrimination within the instrument in favour of heavier isotope, and to allow for it, the Ar^{40}/Ar^{36} values obtained from the commercial 'tank' argon are used to determine the mass discrimination correction.

Fig. (12) shows the procedure sheet for Run No. 136 and the calculation of the age from the spectrometer chart, in this case based on digital voltmeter readings, is given on page 126.

Analyses of the K_2O content of the samples was carried out gravimetrically (and checked flame photometrically) using J. Lawrence Smith fusion and tetraphenylboron precipitation.*

Argon extraction methods are discussed fully by Baadsgaard et al (1957) and the J. Lawrence Smith determination by Goldich and Oslund (1956).

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* Analyses by A. Stelmach, Rock Analysis Laboratory, University of Alberta.

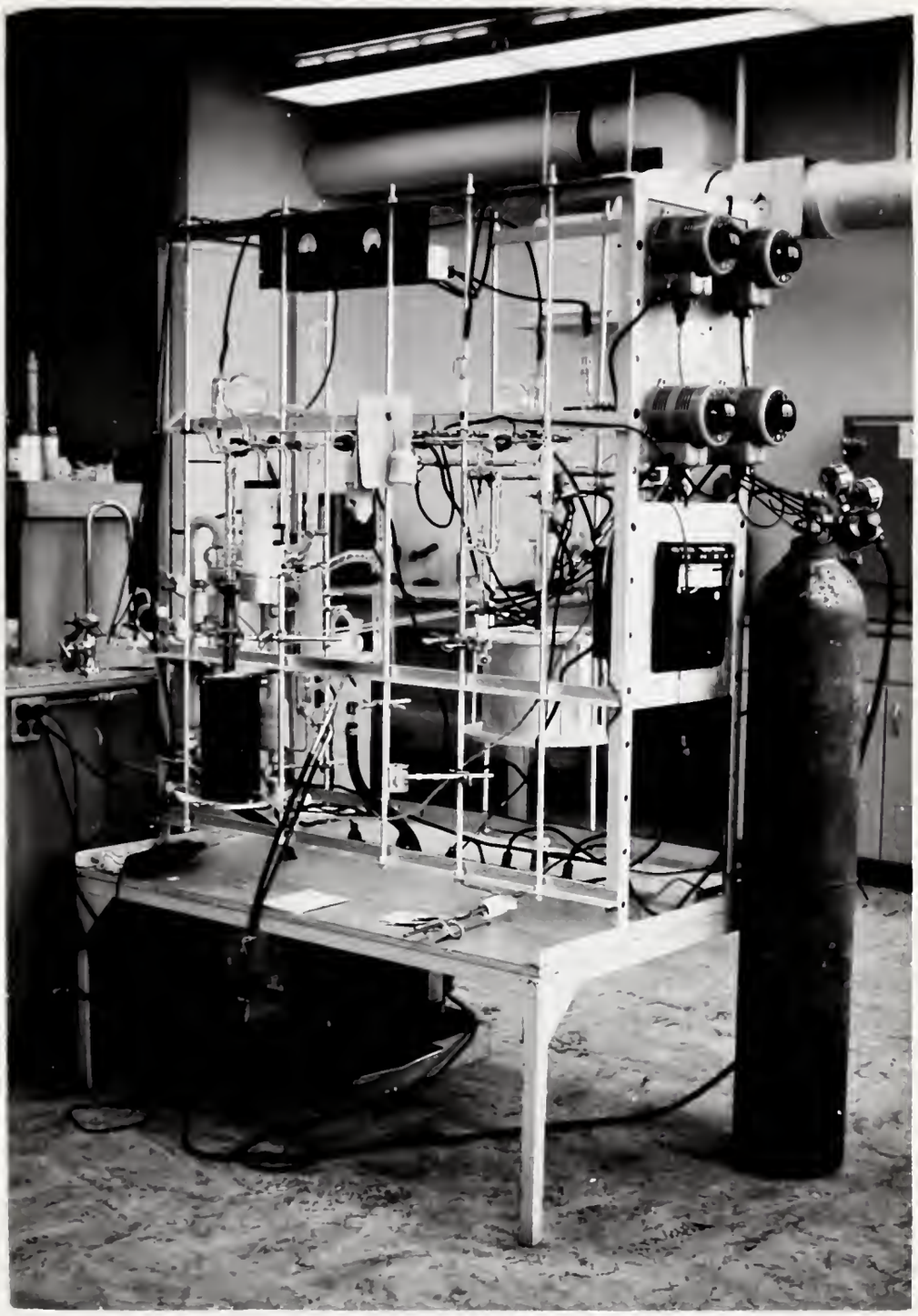

FIGURE 10.

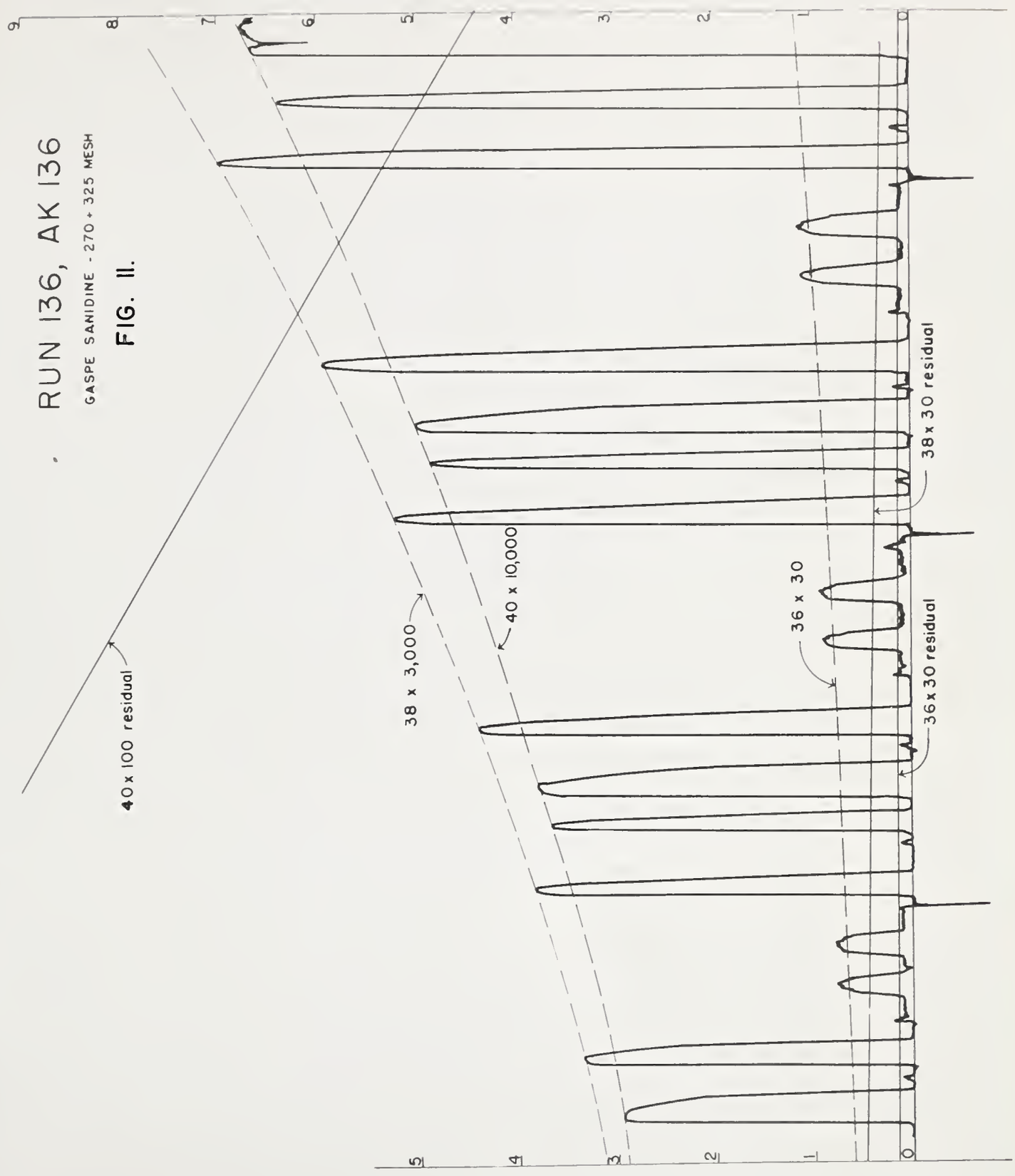
RUN 136, AK 136
GASPE SANIDINE - 270 + 325 MESH
40 x 100 residual
38 x 3,000
40 x 10,000
36 x 30
38 x 30 residual
36 x 30 residual

FIG. 11.

CALCULATION OF THE ABSOLUTE AGE:-

Run 136 AK-136

Gaspe sanidine, -270+325 mesh
Sample weight = 1.089_8 grams
Spike No. 29 IX = $4.12_8 \times 10^{-5}$ cc STP Ar^{38}
K_2O = 6.96%

Ar^{40}:- Measured Ar^{40} - (Ar^{40} from air contamination + spike Ar^{40} + residual Ar^{40}) = radiogenic Ar^{40}

Ar^{38}:- Measured Ar^{38} - (Ar^{38} from air contamination + residual Ar^{38}) = spike Ar^{38}

Ar^{36}:- Measured Ar^{36} - (spike Ar^{36} + residual Ar^{36}) = Ar^{36} from air contamination

Ar^{40}:- 6.07 x 10,000 - (1030+4970+580) = 54,120

(1) Ar^{38}:- 6.93 x 3,000 - (0 + 10) = 20,780 $\frac{Ar^{38}}{Ar^{40}} = 0.384_2$

Ar^{36}:- 1.08 x 30 - (25.1 + 3.9) = 3.4

Ar^{40}:- 4.62 x 10,000 - (970+3,700+800) = 40,730

(2) Ar^{38}:- 5.16 x 3,000 - (0 + 12) = 15,468 $\frac{Ar^{38}}{Ar^{40}} = 0.380_0$

Ar^{36}:- 0.87 x 30 - (18.7 + 4.2) = 3.2

Ar^{40}:- 3.57 x 10,000 - (940+2,820+1,000) = 30,940

(3) Ar^{38}:- 3.93 x 3,000 - (0 + 14) = 11,776 $\frac{Ar^{38}}{Ar^{40}} = 0.380_7$

Ar^{36}:- 0.73 x 30 - (14.3 + 4.5) = 3.1

Average value $\frac{Ar38}{Ar^{40}} = 0.381_6$

$\frac{Ar^{38}}{Ar^{40}} = 0.381_6 \times 1.011 = 0.385_6$ (mass spectrometer mass discrimination correction)

$$\frac{Ar^{40}}{\text{Grm. sample}} = \frac{4.12_8 \times 10^{-5}}{0.385_6 \times 1.089_8} = 9.83 \times 10^{-5} \text{ cc STP}$$

p.p.m. $Ar^{40} = 1.784_6 \times 10^3 \times 9.83 \times 10^{-5} = 0.175_3$

pp.p.m. $K^{40} = 6.98$

$$\frac{Ar^{40}}{K^{40}} = 0.0251_3$$

$$t = 4.30_8 \times 10^9 \log \left[1 + 0.0251_3 (9.08)\right] = 384 \times 10^6 \text{ years}$$

Department of Geology, Geochemistry
University of Alberta

POTASSIUM-ARGON

Run No. 136 AK No. 136 Description: Sanidine - Gaspe (3854-5) -270+325 mesh

Sample Wt. 1.0898 gm.

Spike No. 29 IX

I Preparation

- ☒ Flux (10 × Sample Wt.)
- ☒ Sample (+ filter)
- ☒ Spike
- ☒ Getter
- ☒ Steel Balls
- ☒ C-trap
- ☒ Leak testing
- ☒ Pumps
- ☒ Heaters

Outgassing 35 hrs. Torching: ±1 x whole F - train

II Fusion

- ☒ Cool flux
- ☒ Seal F-train
- ☒ Drop sample
- ☒ Start fusion (~~55~~ 52v)
- ☒ Introduce Spike Argon
- ☒ Trap H_2O

III Transfer

- ☒ H_2O trapped with liq. N_2
- ☒ Seal off from pumps
- ☒ Drop furnaces from Ni-crucible & $Mg(ClO_4)_2$
- ☒ Break seal
- ☒ Short cleanup to TG_1=
- ☒ Liq. N_2 on C-trap, 30 min.
- ☒ Seal off P-train
- ☒ Heat C-trap

IV Purification

- ☒ Preliminary cleanup to TG_1= 50
- ☒ Gettered 3 hrs. to TG_1= 198 (is max.)
- ☒ W-filament on hr.
- ☒ Sample trapped out 20 minutes

V Notes

Fusion - overnight at 450-500°C.
+ 1 hr. at 600°C.
No 'spray-up' apparent
Very rapid clean-up. Clean gas sample.

FIGURE 12

The derivation of the formula for calculating a K/Ar age is shown below.

If the original amount of K^{40} present when the mineral crystallized is denoted by N_o^{K40},

the amount of Ar^{40} present after a period of time t by N_t^{A40},

and the amount of K^{40} present after a period of time t by N_t^{K40},

then $$N_t^{Ar40} = (N_o^{K40} - N_t^{K40}) \cdot \frac{\lambda e}{\lambda e + \lambda \beta} \quad \ldots\ldots\ldots\ldots (1)$$

where λe = the rate of decay of K^{40} to Ar^{40}

and

where $\lambda \beta$ = the rate of decay of K^{40} to Ca^{40}

Now $$N_t^{K40} = N_o^{X40} \cdot e^{-(\lambda e + \lambda \beta)t}$$

and $\therefore$ $$N_o^{K40} = N_t^{K40} \cdot e^{(\lambda e + \lambda \beta)t} \quad \ldots\ldots\ldots\ldots (2)$$

Thus substituting (2) in (1),

$$N_t^{Ar40} = (N_t^{K40} e^{(\lambda e + \lambda \beta)t} - N_t^{K40}) \frac{\lambda e}{\lambda e + \lambda \beta}$$

and $\therefore$ $$N_t^{Ar40} = N_t^{K40} (e^{(\lambda e + \lambda \beta)t} - 1) \frac{\lambda e}{\lambda e + \lambda \beta}$$

$\therefore$ $$\frac{N_t^{Ar40}}{N_t^{K40}} = (e^{(\lambda e + \lambda \beta)t} - 1) \cdot \frac{\lambda e}{\lambda e + \lambda \beta}$$

$\therefore$ taking logarithms,

$$\ln \frac{N_t^{Ar40}}{N_t^{K40}} \cdot \frac{\lambda e + \lambda \beta}{\lambda e} + 1 = (\lambda e + \lambda \beta)t$$

and $\therefore$ $$t = \frac{1}{\lambda e + \lambda \beta} \cdot \ln \frac{N_t^{Ar40}}{N_t^{K40}} \cdot \frac{\lambda e + \lambda \beta}{\lambda e} + 1 \quad \ldots (3)$$

The constants and pertinent data used in this work are as follows:-

$$\lambda e = 0.589 \times 10^{-10}/yr \qquad \lambda \beta = 4.76 \times 10^{-10}/yr$$

'spike' argon:-

$$\frac{Ar^{36}}{Ar^{38}} = 0.00121 \pm 0.00001 \qquad \frac{Ar^{40}}{Ar^{38}} = 0.239 \pm 0.002$$

Atmospheric argon

Ar^{40}	=	99.600 Atomic %	(Nier, 1950)
Ar^{38}	=	0.063 Atomic %	
Ar^{36}	=	0.337 Atomic %	
$\frac{Ar^{40}}{Ar^{36}}$	=	302.0	(Measured from 'tank' argon)

$$\therefore \text{true ratio} = \left(\frac{Ar^{38}}{Ar^{40}}\right)_{measured} \times 1.011$$

(correction made for instrumental mass discrimination)

Abundance of K^{40} (A.E.C. Nuclear Data Tables, 1959)

$$\frac{K^{40}}{K} = 0.0118 \text{ Atomic \%}$$

$$\frac{K^{40}}{K} = 0.0120_7 \text{ weight \%}$$

p.p.m. K^{40}:- $1.002_2 \times \%K_2O$

p.p.m. Ar^{40}:- $1.784_6 \times 10^3 \times$ cc STP Ar^{40}/grm.

Substituting for the constants λe, $\lambda \beta$ and changing to common logarithms in (3),

$$t = 4.30_8 \times 10^9 \log \left[\frac{Ar^{40}}{K^{40}} \cdot 9.08 + 1\right]$$

RESULTS

The results of age determinations on seven different separates are shown in Table (10).

All potassium-bearing materials present in the rock were dated, although from the experience of Folinsbee and Baadsgaard it was expected that the clay and quartzo-feldspathic aggregates (which have a certain amount of the clay material intimately associated with them) would give somewhat lower ages than the sanidine and biotite. This fact is readily understood in view of the very finely crystalline character of the clay and imperfectly crystallized nature of the aggregates, from which loss of argon by simple diffusion might be expected to be much greater. Otherwise the results are extremely consistent and show no variation outside the limits of accuracy of the method (which is taken as $\pm 5\%$). Also worthy of note is the fact that there is no systematic variation in the age obtained with decreasing grain size. This indicates that for the size fractions involved there is no significant differential loss of argon. This conclusion is supported by the results of a study of argon leakage by Baadsgaard *et al* (in press).

TABLE (10)

K/Ar AGES FOR UPPERMOST LOWER DEVONIAN BENTONITES, BELOW LIGHTHOUSE, SHIPHEAD, GASPE PENINSULA

No.	Mineral	Mesh	European Sub-stage	K^{40} ppm*	Ar^{40}/K^{40}	Date m.y.
AK-120	Sanidine	-120+270	Lower Coblenzian	9.18	0.0260	$394 \pm 5\%$
AK-136	Sanidine	-270+325	Lower Coblenzian	6.98	0.0251	$384 \pm 5\%$
AK-137	Sanidine	-325	Lower Coblenzian	5.43	0.0253	$387 \pm 5\%$
AK-113	Biotite	+325	Lower Coblenzian	4.01	0.0240	$376 \pm 7\%$
AK-138	Biotite	-325	Lower Coblenzian	3.90	0.0253	$388 \pm 7\%$
AK-52	Qtz. Fels. Aggs.	-60+120	Lower Coblenzian	4.90	0.0221	$342 \pm 5\%$
AK-106	Mixed layer clay	-35+120	Lower Coblenzian	4.74	0.0209	$325 \pm 5\%$

Constants: $= 0.589 \times 10^{-10}/yr$; $\beta = 4.76 \times 10^{-10}/yr$; $K^{40}/K = 0.0118$ atomic per cent.

* Potassium analyses by A. Stelmach, Rock Analysis Laboratory, University of Alberta.

INTERPRETATION OF RESULTS

The K/Ar ages obtained from the cogenetic sanidine and biotite from Gaspe are in agreement with 'the minimum age for the Lower Devonian' obtained by Hurley et al (1959), from the Seboomook Slate in Maine. In this case the age obtained clearly reflects the time of intrusion of a quartz monzonite body metamorphosing the slate, which is also of Oriskany age. Thus on this evidence the Oriskany is certainly older than 360 m.y. The suggested age for the Gaspe material is in accord with the revised time scale of Holmes (1959) and further is supported by a number of dates averaging 385 m.y., obtained for intrusions cutting Lower Devonian sediments in the New England and Acadian areas (Hurley et al, 1958; Alcock, 1935).

In recent years important differences of opinion have developed, amongst persons engaged in geochronological studies, concerning the validity of the Holmes B time scale, and in particular the duration of the Devonian period. This aspect is discussed by Hurley et al (1958) who point out that K/Ar and Rb/Sr ages for intrusions cutting Lower Devonian strata in the Maine and Nova Scotia areas, range from 350-390 m.y. Furthermore, the Quincy batholith granite, which is considered to have been unroofed in Pennsylvanian times, since boulders of the granite occur in a basal conglomerate

of this age, gave a date of 250 m.y. After pointing out that this would indicate that the Pennsylvanian is younger than 250, the writers suggested that the Devonian may therefore have lasted over 100 m.y. Such an interpretation depends, of course, upon the interval between intrusion and the erosion of the granite being considerable, and the Mississippian period lasting less than 50 m.y., both of which may or may not be true.

At about the same time, however, Folinsbee and Baadsgaard (1958) succeeded in dating a bed of bentonite lying within the Exshaw Shale. This shale can be placed, on very good palaeontological grounds at or very near the boundary of Devonian and Mississippian systems. (Crickmay, 1952; Warren, 1956). The material dated (sanidine) gave an age of 250-280 m.y. which certainly supported the conclusions of the M.I.T. group regarding the extended span of Devonian time.

More recent work has, however, produced a considerable amount of contrary evidence. Cobb and Kulp (1960) obtained a (minimum) U/Pb age of 350 $\pm$ 10 m.y. for a black bituminous shale in the Gassaway Member of the Chattanooga Shale, which is considered to be of uppermost Devonian age. This sequence is, however, not ideal for dating purposes, being considerably condensed and possibly incomplete. (Weller, 1948; Hass, 1956). The same criticism might be applied to the age of 340 m.y.

obtained from a biotite-bearing bentonite which occurs in the Doweltown Member of the Chattanooga Shale (Faul and Thomas, 1959).

Perhaps the main body of evidence against the extension of Devonian time comes from the dating of Carboniferous rocks. Faul, (1957) using the Rb/Sr method found micas from pre-Variscan but post-Tournaisian granites gave ages from 330 to 345 m.y. (The K/Ar method, however, gave lower ages and greater scatter). Zircon dates from the same granite are discordant and give ages that suggest that they have been recycled. Urananite from the post Lower Westphalian Granites of Cornwall gave Darnley (1959) a figure of 288 m.y., whilst Holmes (1948) had earlier found that monazite from another Cornish granite gave him a 'chemical age' (i.e. uncorrected for inherited lead) of 290 m.y. - a figure which, at the time, he took to indicate that monazite was an unreliable timekeeper. The Dartmoor granite biotite has given K/Ar ages of 275 $\pm$ 10 m.y. (Kulp, 1959) and 290 m.y. (Faul, 1959). Furthermore, a recent application of the Rb/Sr method to the Exshaw sanidine has given an age of 345 m.y.

The weight of evidence seems to be against the extension of the Devonian period. However, in accepting this fact, it is important to determine the cause of the erroneous dates furnished by the Quincy

and Exshaw material. In the former case, the writer is not in a position to make any critical re-appraisal of the evidence. The Exshaw bentonite was, however, one of the earliest dated in this department, and since that time a considerable number of sanidine and biotite pairs have been obtained from bentonites and have given reliable dates. It is now becoming possible to make comparative studies of these minerals. It is well known that the term sanidine covers high temperature feldspar with a wide range of optical properties, and chemical composition, and it may possibly be found that certain types of sanidine favour argon retention more or less completely, whilst others are more like the potash feldspars, orthoclase and microcline, in leaking a considerable proportion of the radiogenic gas.

In an effort to obtain evidence of this nature and to compare the Gaspe sanidine with others previously dated, the writer has collected and added to the data on seven such sanidines. This work is described more fully in the appendix to this thesis. Whilst no definite conclusions can be drawn from the information put together, the differences in the various feldspar separates examined are quite apparent and it is held that, with more data of this kind, the significance of the variations with respect to argon retentivity may become apparent.

A careful re-examination of the Exshaw material was considered particularly necessary in view of the

controversial age obtained. A count of 500 grains showed that 45% of the material is what Folinsbee and Baadsgaard (1958) referred to as 'quartz-sanidine intergrowths'. As noted previously, material of similar appearance occurs in the Gaspe bentonites, and has been shown to give an age considerably lower than that of the sanidine. Furthermore, the theoretical potash content of the Exshaw sanidine, as calculated by the X-ray method of Orville (1958), indicates that these intergrowths must have a very high potash content, and, if they are not 100% argon retentive, will have a much greater effect in lowering the age obtained than when they are potash-poor (as must be the case with the Gaspe material in view of the closer correspondence between the X-ray and J. Lawrence Smith potash determinations). It is unfortunate that this critical Exshaw sanidine is one of the few not accompanied by a cogenetic biotite against which the age obtained could be checked.

Leaving the age of the upper boundary of the Devonian system not conclusively settled but probably in excess of 345 m.y., it is clear that the lower boundary must be extended back to about 400 m.y. Since cogenetic sanidine and biotite from Middle Ordovician Kinnekulle bentonites give concordant ages of about 450 m.y. (Folinsbee, Baadsgaard and Lipson, 1960b) it

will be noted that the Silurian period becomes rather short and accepting for the moment the age of 350 m.y. for the Upper Devonian boundary, much shorter than the Devonian. (Fig. 13 shows the revised time scale of Holmes (Holmes, 1959)).

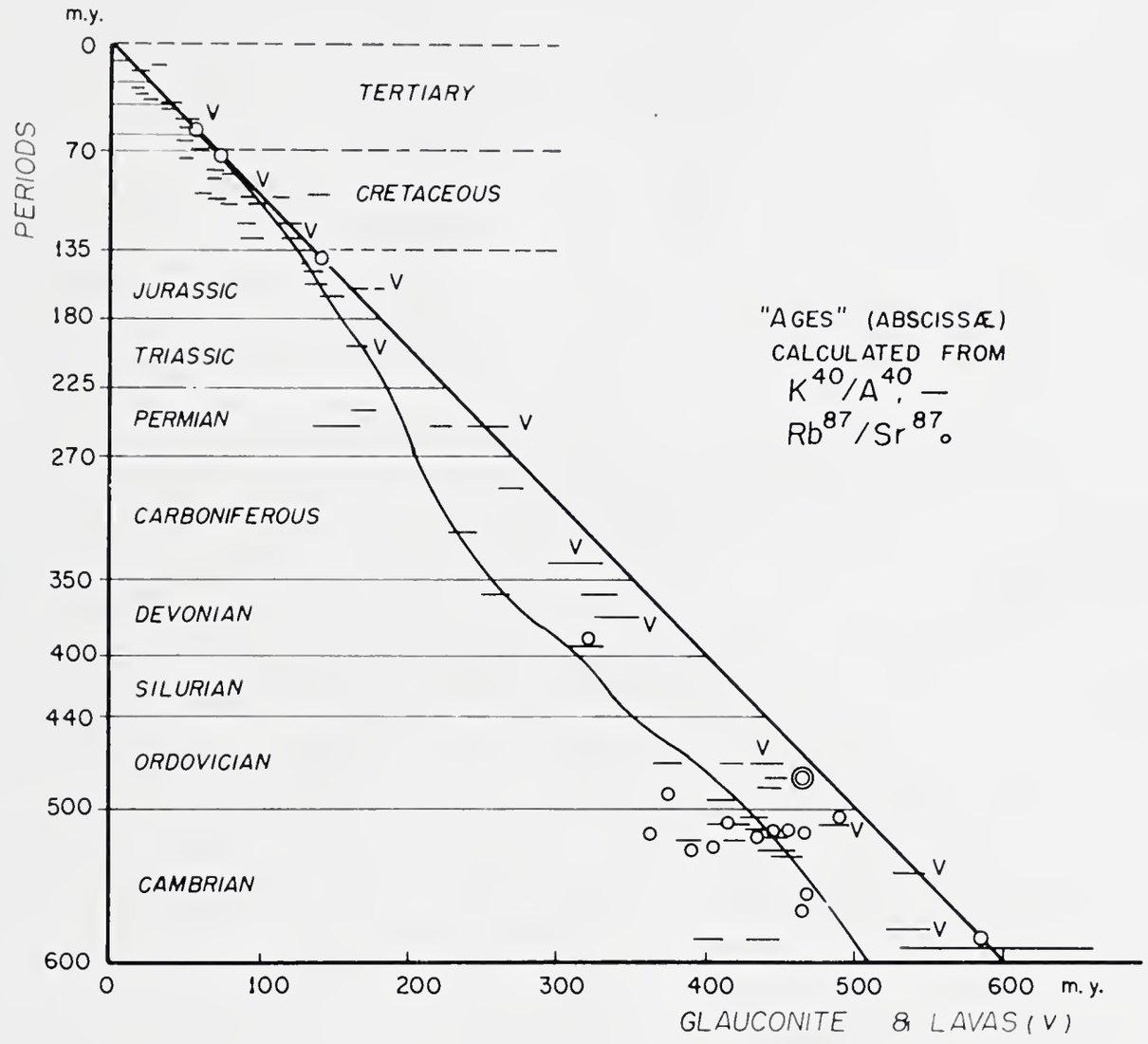

FIGURE 13. The 1947 "B scale" and the 1959 scale are plotted against the latter (shown vertically on the right), together with the K/A and Rb/Sr ages of glauconites and lavas of known stratigraphical horizons. (After Holmes, 1959.).

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A P P E N D I X

CALCULATION OF THE C.I.P.W. NORM FOR 3854-6 SAND FRACTION

.8960 mol quartz	= 53.76%	Q	
.0257 mol or	= 14.29%		
.0074 mol ab	= 3.88%	F	Sal. = 89.93%
.0371 mol an	= 10.31%		
.0754 mol C	= 7.69%	C	
.0660 mol hy	= 6.60%	hy	
.0039 mol mt	= 0.90%		
.0025 mol il	= 0.38%	M	
.0033 mol hm	= 0.53%		fem. 9.08% *
.0040 mol py	= 0.46%		
.0098 mol cc	= 0.98%	A	
.0006 mol ap	= 0.20%		

$$\frac{sal.}{fem.} = \frac{89.93}{9.08} =$$ (therefore the rock belongs to Class 1)

$$\frac{Q}{F} = \frac{59.76}{28.48} = 2.09$$ (Order 2)

$$\frac{K_2O + Na_2O}{CaO} = \frac{.0257 + .0074}{.0489} = .377$$ (Rang 4)

$$\frac{K_2O}{Na_2O} \quad \frac{.0257}{.0074} = 3.47$$ (Sub-Rang 2)

Classification of rock:-

Class 1, Order 2, Rang 4, Sub-Rang 2

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* The carbonate in this rock is not regarded as primary, but as coming from organic contamination of the bentonite. It is therefore disregarded in calculation of the norm.

TABLE (11) - NORMATIVE COMPOSITION OF 3854-6 SAND FRACTION

	Weight %	mol	ap	pr	il	cc	or	ab	an	C	mt	hm	hy	Q
SiO_2	74.09	1.234_8					.1542	.0444	.0742				.0660	.8960
Al_2O_3	14.85	$.145_6$					.0257	.0074	.0371	.0754				
Fe_2O_3	1.15	$.007_2$									.0039	.0033		
FeO	0.75	$.010_4$		.0040	.0025						.0039			
MnO	0.02	-												
MgO	2.64	$.066_0$											.0660	
CaO	2.74	$.048_9$	.0020			.0098			.0371					
Na_2O	0.46	$.007_4$						.0074						
K_2O	2.42	$.025_7$					.0257							
TiO_2	0.18	$.002_5$			.0025									
P_2O_5	0.09	$.000_6$	.0006											
CO_2	0.43	$.009_8$				.0098								
S	0.26	$.007_8$		.0081										

A COMPARISON OF SEVEN SANIDINES USED FOR K/Ar DATING

EXSHAW SANIDINE:- (AK No. 104)

Absolute age: 268 m.y.

General information (As reported by Folinsbee)

Source Material:- The Exshaw bentonite, Alberta. (See "An absolute age for the Exshaw Shale", Folinsbee, R.E., and Baadsgaard, H., A.S.P.G. field trip guide book, 8th Annual Field Conference, Nordegg, p.69-73, 1958).

Location:- Railway cut beneath bridge on highway No. 11 east of Nordegg. A bentonite band in the upper part of the Exshaw shale, about 6" below Tornoceras zone horizon, 1"-4" thick.

Separation:- Non-magnetic fraction at 1.7A, tilt 3°. Specific gravity less than 2.57, greater than 2.54. -100 +140 (U.S. sieve mesh) fraction.

Optical data:- "2V very small, negative, cleavage fragments. Many grains cloudy with carbonaceous films; other grains appear to be devitrified sanidine-rich glass. Not too prepossessing in appearance." (Folinsbee).

Results of count of 500 grains:- (Smith)

Mineral	No. of grains	%
Sanidine	269	53.8
Quartzo-feldspathic aggregates	225	45.0
Quartz	4	.8
Others	2	.4
	500	100.0

The quartzo-feldspathic aggregates are coated with a brown material - probably a clay mineral. Because of the coating it is difficult to say that some of these grains are not sanidine. However, if the coating is a clay mineral then it is more probable that it is coating' the aggregates, which it is believed, alter to the clay. These aggregates may represent what was originally a highly potassic glass which has recrystallized.

Chemical data:-

K_2O = 12.77% (Uncorrected for impurities)

Rb_2O = 0.01_8% (Uncorrected for impurities)

BaO = 0.12_1% (Uncorrected for impurities)

X-ray data:- (Orville's method)

Average value for percentage of the Or molecule = 71.8

Average value for K_2O content = 12.16%

Comments:-

If 45% of the separate consists of quartzo-feldspathic aggregates, then these must be very potassic rich, for the uncorrected % of K_2O determined by chemical analysis is greater than that determined by the X-ray method of Orville. In all other sanidines examined this latter value was somewhat larger than even the corrected chemically determined K_2O content. The aggregates, which are but poorly crystallized material, may well not be as retentive

of radiogenic argon as the sanidine. The higher the potash content of the aggregates the more significant any argon losses that occur. It is quite possible that this fact explains the unexpectedly low age given by the sample.

BEARPAW SANIDINE:- (AK No. 93)

Absolute age:- 75 m.y.

General information (As reported by Folinsbee)

Source Material:- Bentonite No. 1, Lethbridge. Upper Campanian (Cretaceous), Russel and Landes, G.S.C. Mem. 221.

Location:- Bentonite bed on west side of Oldman River at Lethbridge, a few hundred feet downstream from railroad trestle.

Separation:- Non-magnetic fraction at 1.7A, tilt 3°. Specific gravity less than 2.55 (centrifuged) -100 +170 (U.S. sieve mesh) fraction.

Optical data:- "Essentially sanidine feldspar with 15-20% gypsum or anhydrite as contaminant. A little devitrified glassy groundmass, high in quartz-feldspar as further contaminant. Feldspar all negative, most 2V's low, a few seem high for sanidine (possibly anorthoclase in part)." (Folinsbee).

Result of count of 500 grains:- (Smith)

Mineral	No. of grains	%
Sanidine	379	75.8
Anhydrite	44	8.8
Leached mica	51	10.2
Quartz	23	4.6
Others	3	.6
	500	100.0

The leached mica is considered as having lost all its potassium for the purpose of calculating the correction to the chemically determined K_2O content of the sanidine.

Chemical data

K_2O (uncorrected)	= 10.54%
K_2O (corrected for 24.2% impurities)	= 13.47%
Rb_2O	= .00%
BaO (uncorrected)	= 0.30_8%
BaO (corrected for 24.2% impurities)	= 0.40_7%
% Or molecule	= 79.61
% Celsian molecule	= 1.00

X-ray data (Orville's method)

Average value for percentage of the Or molecule = 88.5

Average value for K_2O content = 14.98%

STRAWBERRY CREEK KNEEHILLS BENTONITE SANIDINE:- (AK No. 102-P)

Absolute age: 68 m.y.

General information (As reported by Folinsbee)

Source Material:- Bentonite, Kneehills zone. Bentonite above Kneehills tuff on Strawberry Creek, about Byrne 7 zone.

Location:- Strawberry Creek, Alberta, LSD4, Sec. 5, Tp. 50, Range 1W5

Separation:- Non-magnetic fraction at 1.5A, tilt 0°, specific gravity less than 2.57 (centrifuged twice) -80 +170 (U.S. sieve mesh) fraction.

Optical data:- "An exceptionally clean sample of pure clear sanidine, 2V 10°- 15°, biaxial negative. A few carbonaceous films. Trace of white mica (talc?). Should run 12% K_2O. Sanidine all in cleavage fragments of uniform size. A very superior sample." (Folinsbee).

Results of count of 500 grains:- (Smith)

Mineral	No. of grains	%
Sanidine	422	84.4
Quartz	65	13.0
Clay	6	1.2
Plagioclase	2	0.4
Organic	3	0.6
Carbonate	2	0.4
	500	100.0

The clay may contribute something towards the potash content, but in quantity it will be insignificant; similarly the plagioclase. The main contaminant, quartz is quite innocuous.

Chemical data

K_2O (uncorrected)	= 10.45%
K_2O (corrected for 15.6% impurities)	= 12.39%
Rb_2O	= 0.0 %
BaO (uncorrected)	= 1.144%
BaO (corrected for 15.6% impurities)	= 1.356%
% Or molecule	= 63.21
% Celsian molecule	= 3.32

X-ray data (Orville's Method)

Average value for percentage of the Or molecule = 77.6

Average value for K_2O content = 13.14%

MILLCREEK SANIDINE:- (AK No. 98)

Absolute age: 95 m.y.

General information (As reported by Folinsbee)

Source material:- Six inches of gray-brown biotite-rich soft bentonite in Crowsnest Volcanics horizon, about 200 feet below Inoceramus labiatus zone.

Location:- LSD5-6, Sec. 25, Tp. 5, Rge. 2W5 Beaver Mines sheet 739A on N-S stretch of Millcreek. Marked by blaze on poplar.

Separation:- Non-magnetic fraction at 1.7A, tilt 5°, specific gravity less than 2.57. Washed and dry screened.

Optical data "A very pure sanidine, low 2V, no evidence of alteration or contaminants, except possibly a trace of kaolin. An excellent material for dating." (Folinsbee).

Results of count of 500 grains:- (Smith)

Mineral	No. of grains	%
Sanidine	472	94.4
Quartz	27	5.4
Organic	1	0.2
	500	100.0

Thus the separate contains no significant quantity of potassium-bearing contaminants.

Chemical data

K_2O (uncorrected)	= 10.67%
K_2O (corrected for 5.6% impurities)	= 11.34%
Rb_2O	= 0.0%
BaO (uncorrected)	= 0.127%
BaO (corrected for 5.6% impurities)	= 0.135%
% Or molecule	= 67.01
% Celsian molecule	= 0.33

X-ray data (Orville's Method)

Average value for percentage of the Or molecule = 73.9

Average value for K_2O content = 12.52%

Comments

It will be noted that this sanidine shows a much slighter enrichment in Ba than the sanidine from the Crowsnest Volcanics, probably showing that it is somewhat later in age than horizon from which the volcanic sanidine was obtained.

GASPE SANIDINE:- (Smith)

Absolute age: 386 m.y.

General information

Source material:- Lower Devonian bentonites (3854-6, Gaspe)

Location:- Uppermost bentonite in Shiphead Member, directly below Shiphead lighthouse, Cape Gaspe, Gaspe, P.Q.

Separation:- Non-magnetic fraction at 1.7 A, tilt 1/2°. (Re-cycled approximately twenty times). Specific gravity less than 2.55, greater than 2.45. -270 +325 (U.S. sieve mesh).

Optical data 2V small, negative. Angular grains (mainly cleavage fragments), quite unaltered. Contaminated with some quartz and quartzo-feldspathic aggregates.

Results of count of 500 grains:- (Smith)

Mineral	No. of grains	%
Sanidine	310	62.0
Quartz	110	22.0
Quartzo-feldspathic aggregates	68	13.6
Others	12	2.4
	500	100.0

The quartzo-feldspathic aggregates have very very little clay material associated with them.

Chemical data

K_2O (uncorrected for impurities)	= 7.57%*
K_2O (corrected for 38% impurities)	= 12.21%
Rb_2O	n.d.
BaO (uncorrected for impurities)	= 0.008
BaO (corrected for 38% impurities)	= 0.142
% Or molecule	= 72.1
% Celsian molecule	= 0.34

X-ray data (Orville's method)

Average value for percentage of the Or molecule = 72.3

Average value for K_2O content = 12.24%

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*) Determination carried out by P. Ness, using wet chemical decomposition and tetraphenylborate precipitation.

Comments The correspondence between the K_2O content as determined by the X-ray and chemical methods, is particularly close in this case.

KINNEKULLE SANIDINE:- (AK No. 146)

Absolute age: 440 m.y.

General information (As reported by Baadsgaard)

Source material:- Bentonite

Location:- Kinnekulle bentonite prospect, Sweden

Separation:- Non-magnetic at 1.7A, tilt 1/2°, specific gravity less than 2.55, greater than 2.45.

Optical data (Byström, 1956)

Or	Ab	n_α	n_β	n_γ	2V	Orientation
75	25	1.519	1.523	1.524	15°-18°	$\alpha \wedge a = 3°$ $\beta = b$

Result of count of 500 grains (Smith)

Essentially a pure separate with less than 1% impurities.

Chemical data

K_2O (uncorrected for impurities)	= 12.08
Rb_2O (uncorrected for impurities)	= .00
BaO (uncorrected for impurities)	= 0.49_9

X-ray data (K.A.W. Crook, Orville's Method)

Average value for percentage of the Or molecule = 75.0

Average value for K_2O content = 12.69

CROWSNEST SANIDINE (AK No. 147)

Absolute age: 94 m.y.

General information (As reported by K.A.W. Crook)

Source material:- Upper Albian or lower Cenomanian sanidine-aegirine augite trachyte

Location:- Road cut west of Coleman on Hwy 3 Alta. in Crowsnest Volcanics.

Separation:- Non-magnetic fraction (recycled).

Optical data A very pure sample, the only contaminants being a brownish coating on some of the grains, and a very few grains of the fine grained volcanic matrix in which the sanidine phenocrysts occur. The sanidine has a very variable 2V (19.9° perpendicular to (010) to 24.4° parallel to (010)). Because of the purity of the sample no count of 500 grains was carried out. The impurities are estimated at 1%.

Chemical data (by A. Stelmach)

SiO_2	=	64.21
TiO_2	=	.05
Al_2O_3	=	18.71
Fe_2O_3	=	.37
FeO	=	.12

MnO	=	.01
MgO	=	.03
CaO	=	.01
Na_2O	=	2.34
K_2O	=	12.74
P_2O_5	=	.01
H_2O	=	.23
BaO	=	.69
Rb_2O	=	.02
		99.55

K_2O (corrected for 1% impurities, and water)	= 12.91
BaO (uncorrected)	= 0.690
BaO (corrected for 1% impurities, and water)	= 0.695
% Or molecule	= 76.30
% Celsian molecule	= 1.70

X-ray data (K.A.W. Crook, Orville's method)

Average value for percentage of the Or molecule = 77.5

Average value for K_2O content = 13.10

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